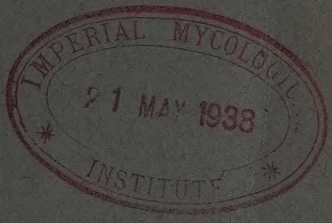
COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1938



VOLUME XVIII

№ 9

ÉDITION DE L'ACADÉMIE DES SCIENCES DE L'URSS
MOSCOU

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21 Mars

COMPTES RENDUS

(DOKLADY)

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NOUVELLE SÉRIE

6-me année

Paraissant tous les dix jours

1938

VOLUME XVIII, № 9

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Rédacteur en chef A. Fersman. Rédacteur S. Bernstein.

En composition 16/III 1938. En impression 16/IV 1938. Nombre de feuilles d'impression 5. Nombre de caractères par feuille d'impression 65000. Pages 617—696. Format du papier 72×110 cm. Tirage 1 300. Moscou. Glavlit B—42762. Numéro d'édition 784. Numéro typographique 469.

Imprimerie № 16. Moscou, Trekhproudnij péréoulok, 9.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

MATHÉMATIQUES

SUR LA MEILLEURE APPROXIMATION DES FONCTIONS CONTINUES DÉRIVABLES SUR TOUT L'AXE RÉEL

Par M. KREIN

(Présenté par S. N. Bernstein, de l'Académie, 14. II. 1938)

Dans cette note nous allons montrer que les résultats récemment obtenus par l'auteur relatifs à la meilleure approximation des fonctions périodiques par des polynômes trigonométriques peuvent être étendus aux fonctions presque-périodiques et même à une classe de fonctions beaucoup plus générale.

1. Soit

$$P(r) = A_0 r^m + A_1 r^{m-1} + \ldots + A_m \qquad (A_0 \neq 0,\ m \geqslant 1)$$

un polynôme réel n'ayant aucune racine purement imaginaire ou égale à zéro. Posons

$$g(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{itx}}{P(it)}\, dt \qquad (-\infty < x < \infty).$$

Il est aisé de voir que 1) $g(x)$ est une fonction réelle, 2) il existe deux constantes $\gamma > 0$, $\sigma > 0$ telles que

$$|g(x)| < \gamma e^{-\sigma|x|} \qquad (-\infty < x < \infty)$$

et 3) quelle que soit la fonction complexe bornée mesurable $h(x)$ $(-\infty < x < \infty)$ l'équation différentielle

$$P(D)\, y(x) = h(x) \qquad (-\infty < x < \infty)$$

possède une et une seule solution bornée* qui est exprimée par la formule:

$$y(x) = \int_{-\infty}^{\infty} g(x - s)\, h(s)\, ds.$$

---

* Nous avons en vue une solution $y(x)$ possédant m dérivées en ce sens que les dérivées $y(x)$, $y'(x)$, ... $y^{(m-1)}(x)$ existent partout et sont des fonctions absolument continues dans tout intervalle fini, et, par conséquent, la dérivée $y^{(m)}(x)$ existe presque partout.

A tout $N>0$ faisons correspondre les fonctions

$$H_N(x)=\sum_{k=-\infty}^{\infty}(-1)^k g\left(x+\frac{k\pi}{N}\right)=\frac{N}{\pi}\sum_{k=-\infty}^{\infty}\frac{e^{(2k+1)Nix}}{P[(2k+1)Ni]},$$

$$F_N(x)=\sum_{k=-\infty}^{\infty}(-1)^k\int_{x+\frac{(k-1)\pi}{N}}^{x+\frac{k\pi}{N}} g(x)\,dx=\frac{2}{\pi i}\sum_{k=-\infty}^{\infty}\frac{e^{(2k+1)Nix}}{(2k+1)P[(2k+1)Ni]}. \quad (1)$$

Comme $F_N(x)$ est une fonction continue périodique: $F_N\left(x+\frac{2\pi}{N}\right)=F_N(x)$ $\left[\text{de plus } F_N\left(x+\frac{\pi}{N}\right)=-F_N(x)\right]$, elle possède un maximum absolu:

$$C_N=\max F_N(x)=-\min F_N(x)=0\left(\frac{1}{N^m}\right).$$

Soit α un point quelconque où le maximum C_N est atteint: puisque $F'_N(x)=2H_N(x)$, on a $H_N(\alpha)=0$.

Envisageons les fonctions:

$$g_N(x)=\frac{\sin N(x-\alpha)}{N}\sum_{k=-\infty}^{\infty}(-1)^k\frac{g\left(\alpha+\frac{k\pi}{N}\right)}{x-\alpha-\frac{k\pi}{N}}$$

et

$$\psi(s)=\begin{cases}\displaystyle\sum_{k=-\infty}^{\infty} g\left(\alpha+\frac{k\pi}{N}\right)e^{\frac{k\pi}{N}is} & \text{pour } |s|\leqslant N,\\ 0 & \text{pour } |s|\geqslant N.\end{cases}$$

On vérifie sans peine que

$$g_N(\alpha+x)=\frac{1}{2N}\int_{-N}^{N}\psi(s)\,e^{-ixs}\,ds,$$

et comme $\psi(N)=\psi(-N)=H_N(\alpha)=0$ on trouve qu'il existe une constante G telle que

$$|g_N(x)|<\frac{G}{x^2}.$$

Dans tout ce qui suit nous supposons que N est suffisamment grand, à savoir *: $N>3^{\varkappa-1}\mu$, où μ est la borne supérieure des parties imaginaires des racines du polynôme $P(r)$, et $\varkappa$ est le nombre total des couples des racines imaginaires de ce polynôme.

Lemme. *La constante N vérifiant la condition indiquée, les seules noeuds de la différence $g(x)-g_N(x)$ se trouvent aux points $x=\alpha+\frac{k\pi}{N}$ $(k=0,\ \pm1,\ \pm2,\ \ldots)$ et par suite*

$$\int_{-\infty}^{\infty}|g(x)-g_N(x)|\,dx=C_N.$$

---

* Il est possible que les résultats qui suivent restent encore valables si l'on impose à N une restriction plus faible, à savoir $N>\mu$.

On peut démontrer ce lemme en le réduisant aux propositions qu'on a établi auparavant (1).

Indiquons encore le fait suivant. Soit $\mathfrak{F}_N$ l'ensemble des fonctions $\varphi(x)$ $(-\infty < x < \infty)$ absolument intégrables sur tout l'axe réel et satisfaisant à la condition

$$\int_{-\infty}^{\infty} \varphi(x)\, e^{i\lambda x} dx = 0 \quad \text{pour } |\lambda| \geqslant N \quad (\lambda \text{ est réel}).$$

Alors

$$C_N = \min_{\varphi \subset \mathfrak{F}_N} \int_{-\infty}^{\infty} |g(x) - \varphi(x)|\, dx.$$

Rappelons encore (1) que, si l'opérateur $P(D)$ ne contient que des puissances impaires de D, on a:

$$C_N = \frac{2}{\pi} \left| \sum_{k=-\infty}^{\infty} \frac{1}{(2k+1)\, P[(2k+1)Ni]} \right|,$$

et s'il ne contient que des puissances paires de D, on a:

$$C_N = \frac{2}{\pi} \left| \sum_{k=-\infty}^{\infty} \frac{(-1)^k}{(2k+1)\, P[(2k+1)Ni]} \right|.$$

2. Soit

$$f(x) \sim \sum_{k=1}^{\infty} c_k e^{i\lambda_k x}$$

une fonction presque-périodique au sens de M. Bohr. Si la fonction $f(x)$ possède m dérivées et si

$$|P(D) f(x)| \leqslant 1, \tag{2}$$

la fonction

$$f_N(x) = \int_{-\infty}^{\infty} g_N(x-s)\, h(s)\, ds, \quad \text{où} \quad h(s) = P(D) f(s)$$

est, comme il est aisé de voir, une fonction presque-périodique et

$$f_N(x) \sim \sum_{k=1}^{\infty} \psi(\lambda_k)\, P(i\lambda_k)\, c_k e^{i\lambda_k x}.$$

Puisque $\psi(s) = 0$ pour $|s| \geqslant N$, les exposants propres de Fourier de la fonction $f_N(x)$ se trouvent à l'intérieur de l'intervalle $(-N, N)$. D'autre part

$$|f(x) - f_N(x)| = \left| \int_{-\infty}^{\infty} \{ g(s) - g_N(s) \}\, h(x-s)\, ds \right| \leqslant$$

$$\leqslant \int_{-\infty}^{\infty} |g(s) - g_N(s)|\, ds = C_N,$$

où le signe d'égalité est atteint pour un $x = x_0$ dans le cas et dans ce cas seulement où l'on a presque partout $h(x) = e^{i\theta} \operatorname{sgn} \sin(\alpha + x_0 - x)$ et par suite $f(x) = f_0(x) = F_N(\alpha + x_0 - x)$, où la fonction périodique $F_N(x)$ est définie par l'égalité (1). Il est important que dans ce dernier cas la fonction $f_N(x)$ s'annule identiquement et, comme il est aisé de montrer, quel que soit le polynôme trigonométrique généralisé $T(x) \not\equiv 0$, dont les exposants se trouvent à l'intérieur de l'intervalle $(-N, N)$, on a l'inégalité:

$$\sup_{-\infty < x < \infty} |f_0(x) - T(x)| > C_N.$$

Pour formuler le théorème qui suit il nous reste encore à faire la remarque suivante.

Si l'on ne suppose plus que le polynôme $P(r)$ n'a pas de racines purement imaginaires ou égales à zéro, on peut encore définir la fonction $F_N(x)$ et, par conséquent, la constante C_N en supprimant dans la formule (1) le terme intermédiaire. De plus on peut toujours dans ce cas remplacer le polynôme $P(r)$ par un polynôme $P_1(r)$, n'ayant pas de racines purement imaginaires ou égales à zéro et dont les coefficients sont si proches de ceux du polynôme $P(r)$ que la constante nouvelle C'_N diffère de C_N d'aussi peu qu'on le veut et que pour la fonction donnée $f(x)$ [bornée et satisfaisant à l'inégalité (2)] on ait l'inégalité $|P_1(D)f(x)| < 1 + \varepsilon$, où ε est une quantité positive arbitraire donnée à l'avance. On arrive ainsi au

Théorème 1. *Si la fonction presque-périodique $f(x)$ possède m dérivées et*

$$|P(D)f(x)| \leqslant 1 \qquad (-\infty < x < \infty),$$

où $P(r)$ est un polynôme réel, il existe pour tout $\varepsilon > 0$ un polynôme trigonométrique généralisé

$$T(x) = \sum_1^q c_k e^{i\mu_k x}$$

dont les exposants se trouvent à l'intérieur de l'intervalle $(-N, N)$ tel que

$$|f(x) - T(x)| < C_N + \varepsilon.$$

Si l'intervalle $(-N, N)$ contient un nombre fini d'exposants de la fonction $f(x)$ ou si le polynôme $P(r)$ n'a pas de racines purement imaginaires ou égales à zéro, la quantité ε dans cette inégalité peut être supprimée *.

La constante C_N est «exacte» **, *si même on omet l'hypothèse que les exposants μ_k du polynôme $T(x)$ appartiennent à la fonction $f(x)$.*

Ce théorème contient comme cas particulier les résultats récents de J. Favard (2), N. Achyeser (3, 4) et de l'auteur (1) relatifs à l'approximation des fonctions périodiques.

3. Désignons par E_N l'ensemble de toutes les fonctions entières possédant la propriété: à toute fonction $\varphi(z) \subset E_N$ il correspond deux constantes $M > 0$ et $\sigma < N$ telles que

$$|\varphi(z)| \leqslant M e^{\sigma|z|}.$$

Le théorème 1 peut être généralisé de la manière suivante.

* Il est possible que la quantité $\varepsilon > 0$ peut être supprimée dans tous les cas.
** C'est-à-dire ne peut être remplacée par une autre plus petite.

Théorème 2. *Si la fonction bornée* $f(x)$ $(-\infty < x < \infty)$ *possède m dérivées et*

$$|P(D)f(x)| \leqslant 1,$$

il existe pour tout $\varepsilon > 0$ *une fonction entière* $\varphi(z) \subset E_N$ *telle que*

$$|f(x) - \varphi(x)| < C_N + \varepsilon.$$

La constante C_N *dans cette inégalité est exacte.*

Si le polynôme $P(r)$ n'a pas de racines purement imaginaires ou égales à zéro, on peut prendre pour $\varphi(x)$ la fonction

$$f_\sigma(x) = \int_{-\infty}^{\infty} g_\sigma(x-s)\, h(s)\, ds \qquad [h(s) = P(D)f(s)],$$

où $\sigma < N$ est assez proche de N.

Si le spectre de la fonction $f(x)$ se trouve à l'extérieur de l'intervalle $(-N, N)$, c'est-à-dire si la transformation généralisée de Fourier [au sens de H. Hahn (5)]:

$$E(\alpha) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x)\, \frac{e^{-i\alpha x} - L(\alpha, x)}{-x^2}\, dx,$$

où

$$L(\alpha, x) = \begin{cases} 1 - i\alpha x & \text{pour } |x| \leqslant 1, \\ 0 & \text{pour } |x| \geqslant 1, \end{cases}$$

est une fonction linéaire à l'intérieur de l'intervalle $(-N, N)$, la fonction correspondante $f_\sigma(x) \equiv 0$ pour $\sigma < N$. On arrive ainsi au

Théorème 3. *Si la fonction bornée* $f(x)$ $(-\infty < x < \infty)$ *possède m dérivées et*

$$|P(D)f(x)| \leqslant 1 \qquad (-\infty < x < \infty),$$

le spectre de la fonction $f(x)$ *se trouvant à l'extérieur de l'intervalle* $(-N, N)$, *on a l'inégalité*

$$|f(x)| \leqslant C_N. \tag{3}$$

La constante C_N *est exacte; le signe d'égalité est atteint pour la fonction* $f_0(x) = e^{i\vartheta} F_n(x - x_0)$.

Dans le cas des fonctions presque-périodiques l'inégalité (3) a été établie par H. Bohr (6) pour l'opérateur $P(D) = D$ et par J. Favard (7) pour l'opérateur $P(D) = D^m$. Tout récemment B. Lewitan (8) en partant du résultat de H. Bohr a obtenu l'inégalité (3) pour le cas d'une fonction $f(x)$ bornée quelconque et $P(D) = D$ *.

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Manuscrit reçu
le 21. II. 1938.

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* D'ailleurs, sa méthode permet d'établir l'inégalité (3) aussi pour $P(D) = D^m$, si l'on s'appuie sur le résultat de J. Favard.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

MATHÉMATIQUES

SUR UNE CLASSE SPÉCIELLE D'OPÉRATEURS LINÉAIRES TOTALEMENT CONTINUS

Par M. A. RUTMANN

(Présenté par S. N. Bernstein, de l'Académie, le 10. II. 1938)

Dans tout ce qui suit E désigne un espace linéaire du type (B) (1).

Soit S un ensemble d'éléments de E satisfaisant aux conditions suivantes:

1. Si l'on a $x \in S$, $y \in S$, on a aussi $x+y \in S$.
2. Si l'on a $x \in S$, $\lambda \geqslant 0$, on a aussi $\lambda x \in S$.
3. L'ensemble S est fermé.
4. Si l'on a $x \in S$, $x \neq 0$, on a aussi $-x \overline{\in} S$.

Désignons d'ailleurs par $\overline{S}$ l'ensemble de toutes les fonctionnelles $f \in \overline{E}$, satisfaisant à la condition

$$f(x) \geqslant 0 \text{ pour tout } x \in S.$$

On a le

Théorème 1. *Soit A un opérateur linéaire totalement continu jouissant des propriétés suivantes:*

a) Si l'on a $x \in S$, on a aussi $Ax \in S$.

b) Il existe un scalaire positif c et un élément $x_0 \in S$ tels que $Ax_0 - cx_0 \in S$.

Ces conditions étant remplies, l'opérateur A possède un vecteur caractéristique e ($Ae = \lambda e$; $\lambda \neq 0$) appartenant à l'ensemble S.

Imposons encore à S la condition suivante.

5. Tout élément de E peut être représenté comme différence de deux éléments de S.

On a alors le

Théorème 2. *L'ensemble S satisfaisant aux conditions 1—5 et l'opérateur A étant le même que dans le théorème 1, l'une des valeurs caractéristiques de l'opérateur A à module maximum est positive et il lui correspond un vecteur caractéristique appartenant à S.*

La condition 5 est certainement remplie, si S contient des points intérieurs. Dans ce cas on a encore le

Théorème 3. *Les conditions du théorème 1 étant remplies et l'ensemble S ayant des points intérieurs, supposons encore que l'opérateur A vérifie la condition suivante: à tout élément frontière $x \in S$ il correspond un entier positif $n = n(x)$ tel que le vecteur $A^n x$ se trouve à l'intérieur de S.*

Dans ce cas l'opérateur A a dans S un et seulement un vecteur caractéristique e ($Ae = \lambda_0 e$). La valeur caractéristique positive λ_0 qui correspond à ce vecteur surpasse le module de toute autre valeur caractéristique. La valeur réciproque $\mu_0 = \frac{1}{\lambda_0}$ est un pôle simple de la résolvante $A(E - \mu A)^{-1}$.

D'ailleurs l'opérateur conjugué $\overline{A}$ possède les mêmes propriétés par rapport à l'ensemble $\overline{S}$.

Faute de place nous omettons les démonstrations des théorèmes 1, 2, 3. Indiquons seulement qu'elles sont basées sur le principe du point invariant de M. Schauder (2) et sur les lemmes suivants:

Lemme 1. *L'ensemble S vérifiant les conditions 1—4, soient x_0 un élément quelconque de S et S_ε l'ensemble de tous les éléments $x \in S$ tels que*

$$x - |x| \varepsilon x_0 \in S \qquad (\varepsilon > 0).$$

Pour tout $\varepsilon > 0$ assez petit, l'ensemble S_ε satisfait encore aux conditions 1 — 4.

Lemme 2. *Dans les mêmes conditions il existe une fonctionnelle linéaire $f(x)$ telle que $f(x) \geqslant 0$ pour $x \in S$ et $f(x) > \delta_\varepsilon > 0$ pour $x \in S_\varepsilon$, $|x| = 1$.*

Lemme 3. *Dans les mêmes conditions il existe un opérateur continu Ux défini dans S tel que*

1) *Si l'on a $x \in S$, on a aussi $Ux \in S_\varepsilon$;*
2) $|Ux| = |x|$;
3) $|x - Ux| < |x| \frac{4\varepsilon}{1-2\varepsilon}$.

Lemme 4. *Si l'opérateur A possède les propriétés a) et b) du théorème 1, on a partout dans S_ε l'inégalité:*

$$|Ax| \geqslant h|x|; \quad h = h(\varepsilon) > 0.$$

Lemme 5. *Si l'opérateur A possède les propriétés a) et b) du théorème 1 et si pour un $x \in S$ on a:*

$$Ax = \alpha x - \beta x_0; \quad \alpha > 0, \ \beta > 0,$$

on a aussi:

$$\alpha \geqslant c.$$

x_0 et c sont ici les mêmes que dans le théorème 1. Outre ces lemmes nous nous servons en démontrant les théorèmes 2, 3 de quelques propriétés de la suite des opérateurs A^n ($n = 1, 2, \ldots$).

Indiquons encore quelques applications des théorèmes 1, 2, 3.

α) Soit, par exemple, E l'espace euclidien à n dimensions. Soit S l'ensemble de tous les vecteurs, dont les composantes dans un système des coordonnées sont non négatives.

Dans ce cas les conditions 1—5 sont remplies et S a des points intérieurs. Il est clair aussi que l'opérateur linéaire A laisse invariant l'ensemble S dans le cas et dans ce cas seulement, où il lui correspond (dans le système des coordonnées choisi) une matrice aux éléments non négatifs. Cela étant, les théorèmes 1, 2, 3 nous amènent dans ce cas aux résultats, obtenus par M. Perron (3) et M. Frobenius (4).

β) Considérons l'espace $C_{(a,b)}$ des fonctions $\varphi(t)$ continues dans l'intervalle (a, b) en définissant la norme par la condition $\|\varphi\| = \max |\varphi(t)|$

$(a \leqslant t \leqslant b)$. Soit maintenant S l'ensemble de toutes les fonctions non négatives. Cela posé, les conditions 1—5 seront encore remplies et S aura des points intérieurs. Considérons l'opérateur

$$A\varphi = \int_a^b K(t,s)\,\varphi(s)\,ds,$$

où le noyau $K(t,s)$ est continu dans le carré $a \leqslant t,\ s \leqslant b$ et satisfait à la condition: $K(t,s) \geqslant 0$ et pour tout t_0 $(a < t_0 < b)$ la fonction de s: $K(t_0,s) \not\equiv 0$.

On peut alors appliquer à l'operateur A les théorèmes 1, 2. On arrive ainsi au théorème de M. Jentsch [5] concernant les noyaux non négatifs avec l'extension indiquée par F. R. Gantmakher [6].

γ) Considérons l'espace de Hilbert ayant pour vecteurs, comme il est bien connu, des suites de nombres réels dont les sommes des carrés sont convergentes. De même que dans α), soit S l'ensemble de tous les vecteurs, dont les coordonnées sont non négatives. Dans ce cas l'ensemble S vérifie les conditions 1—5, mais, comme il est aisé de voir, il n'a pas de points intérieurs. Il correspond à tout opérateur linéaire totalement continu, qui laisse l'ensemble S invariant, une matrice aux éléments non négatifs. En vertu des théorèmes 1, 2 on obtient maintenant le

Théorème. *Soit* $A = \|a_{ik}\|_1^\infty$ *une matrice infinie réelle et totalement continue. Si tous les éléments de cette matrice sont non négatifs et l'un au moins des éléments diagonaux est positif, alors, parmi les plus grandes en valeur absolue valeurs caractéristiques de la matrice* A *il en existe une qui est positive et il lui correspond un vecteur propre aux coordonnées non négatives.*

Ce théorème permet d'étendre les résultats principaux de la théorie des matrices oscillatoires de F. R. Gantmakher et M. G. Krein [7] aux matrices $\|a_{ik}\|_1^\infty$ infinies totalement continues et jouissant de la propriété que tout segment $\|a_{ik}\|_1^\infty$ $(n = 1, 2, \ldots)$ est une matrice oscillatoire.

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Manuscrit reçu
le 13. II. 1938.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

PHYSIQUE MATHÉMATIQUE

SUR L'APPLICATION DE LA REPRÉSENTATION CONFORME À LA RÉSOLUTION DU PROBLÈME PLAN DE LA THÉORIE DE L'ÉLASTICITÉ

Par L. S. GILMAN

(Présenté par B. G. Galerkin, de l'Académie, le 28. I. 1938)

L'application de la représentation conforme à la solution du problème mentionné a été considérée par plusieurs auteurs (Lowe, Muschélišwili et autres) qui ont indiqué diverses méthodes pour résoudre ce problème. Nous allons examiner dans cette note une autre méthode d'application de la représentation conforme, fondée sur l'utilisation des lignes isostatiques. Nous allons profiter des résultats, obtenus par M. P. Neményi[1] qui a démontré que chaque réseau orthogonal formé de deux systèmes conjugués de lignes isothermiques peut être considéré comme un réseau de lignes isostatiques. M. P. Neményi établit en même temps des formules qui permettent de déterminer les tensions principales, correspondant à un système donné de lignes isostatiques. Ces résultats nous donnent la possibilité d'obtenir avec une grande simplicité la solution du problème plan de la théorie de l'élasticité dans certains cas. En effet, si l'on connaît la solution pour un cas quelconque, où les lignes isostatiques forment un réseau isothermique, et si l'on effectue ensuite la représentation conforme du domaine donné sur un domaine limité par un autre contour, on peut obtenir un réseau nouveau de lignes isostatiques, et déduire ensuite la solution du problème pour le nouveau contour.

D'ailleurs un bord, libre d'efforts tangentiels, reste le même dans le nouveau domaine. Un bord, libre d'efforts normaux se transforme en un bord qui n'est pas toujours libre d'efforts normaux. Néanmoins en utilisant la méthode indiquée on peut obtenir des résultats assez importants.

Considérons par exemple un demi-plan chargé d'une force, appliquée à son bord. Les lignes isostatiques présentent dans ce cas un réseau isothermique, formé de rayons et de cercles concentriques. Nous supposons ce demi-plan contenu dans le plan de la variable $u = X + iY$.

La relation $u = \sin \frac{\pi z}{2l}$ fournit la représentation conforme de ce demi-plan sur un domaine ayant la forme d'une bande infinie de largeur $2l$ dans le plan de la variable $z = x + iy$.

Les systèmes de circonférences et de rayons se transforment en systèmes de courbes, définies par les equations suivantes:

$$\frac{1}{2}\ln\left(\sin^2\frac{\pi x}{2l}+\operatorname{sh}^2\frac{\pi y}{2l}\right)=C,$$

$$\operatorname{arctg}\left(\operatorname{ctg}\frac{\pi x}{2l}\operatorname{th}\frac{\pi y}{2l}\right)=C'.$$

En considérant ces systèmes de courbes comme des lignes isostatiques, nous allons déterminer les tensions correspondantes principales σ_1 et σ_2.

Nous allons profiter des formules de M. Neményi.

Posons: $\sigma_1+\sigma_2=2\sigma$; $\sigma_2-\sigma_1=2\tau$.

Soient $\varphi(x,y)=C$ et $\psi(x,y)=C'$ les équations de deux systèmes de lignes isostatiques, formant un réseau isothermique.

Soit $w(z)=\varphi(x,y)+i\psi(x,y)$.

D'après Neményi les valeurs de σ et τ sont déterminées par les formules suivantes:

$$\sigma=\Re\int(2Az+B+iC)\left(\frac{dw}{dz}\right)^2dz; \tag{1}$$

$$\tau=[A(x^2+y^2)+Bx+Cy+D]\left|\frac{dw}{dz}\right|^2; \tag{2}$$

A, B, C, D étant des constantes arbitraires.

Dans le cas que nous examinons, nous avons:

$$\varphi(x,y)=\frac{1}{2}\ln\left(\sin^2\frac{\pi x}{2l}+\operatorname{sh}^2\frac{\pi y}{2l}\right);$$

$$\psi(x,y)=\operatorname{arctg}\left(\operatorname{ctg}\frac{\pi x}{2l}\operatorname{th}\frac{\pi y}{2l}\right);$$

$$w(z)=\ln\left(\sin\frac{\pi z}{2l}\right).$$

Et ensuite:

$$\sigma=2A\left[\frac{1}{2}\ln\left(\sin^2\frac{\pi x}{2l}+\operatorname{sh}^2\frac{\pi y}{2l}\right)-\frac{\pi}{2l}\frac{x\sin\frac{\pi x}{l}+y\operatorname{sh}\frac{\pi y}{l}}{\operatorname{ch}\frac{\pi y}{l}-\cos\frac{\pi x}{l}}-\frac{\pi^2}{8l^2}(x^2-y^2)\right]-$$

$$-\frac{\pi}{4l}B\left(\frac{2\sin\frac{\pi x}{l}}{\operatorname{ch}\frac{\pi y}{l}-\cos\frac{\pi x}{l}}+\frac{\pi x}{l}\right)-\frac{\pi}{4l}C\left(\frac{2\operatorname{sh}\frac{\pi y}{l}}{\operatorname{ch}\frac{\pi y}{l}-\cos\frac{\pi x}{l}}-\frac{\pi y}{l}\right)+E; \tag{3}$$

$$\tau=[A(x^2+y^2)+Bx+Cy+D]\frac{\pi^2}{4l^2}\frac{\operatorname{ch}\frac{\pi y}{l}+\cos\frac{\pi x}{l}}{\operatorname{ch}\frac{\pi y}{l}-\cos\frac{\pi x}{l}}. \tag{4}$$

Nous allons étudier le cas, où toutes les constantes arbitraires, excepté C, sont nulles.

Dans ce cas nous aurons:

$$\sigma_1=\sigma-\tau=-\frac{\pi}{2l}C\frac{\operatorname{sh}\frac{\pi y}{l}+\frac{\pi y}{l}\cos\frac{\pi x}{l}}{\operatorname{ch}\frac{\pi y}{l}-\cos\frac{\pi x}{l}}; \tag{5}$$

$$\sigma_2=\sigma+\tau=-\frac{\pi}{2l}C\frac{\operatorname{sh}\frac{\pi y}{l}-\frac{\pi y}{l}\operatorname{ch}\frac{\pi y}{l}}{\operatorname{ch}\frac{\pi y}{l}-\cos\frac{\pi x}{l}}. \tag{6}$$

Ces expressions correspondent évidemment au cas où la bande est chargée d'une force appliquée à l'origine de coordonnées et dirigée suivant l'axe OY. Les bords latéraux $x = \pm l$ sont soumis à l'action des efforts normaux répartis suivant la relation:

$$q = -\frac{\pi}{2l} C \frac{\operatorname{sh}\frac{\pi y}{l} - \frac{\pi y}{l}\operatorname{ch}\frac{\pi y}{l}}{\operatorname{ch}\frac{\pi y}{l} + 1}.$$

On peut supposer avec une précision suffisante que les efforts normaux, agissant sur les bords latéraux d'une bande longue, ne produisent que des tensions correspondantes X_x qui restent constantes le large de la bande.

La solution obtenue nous permet, par suite, d'étudier les tensions, produites dans la bande par la force appliquée à l'origine de coordonnées.

Les tensions principales étant déterminées il est facile d'obtenir des expressions pour X_x, Y_y et X_y en utilisant les relations bien connues:

$$X_x = \sigma - \tau \cos 2\alpha;\ Y_y = \sigma + \tau \cos 2\alpha;\ X_y = -\tau \sin 2\alpha.$$

Nous désignons ici par α l'angle que fait avec l'axe des x la tangente à la courbe $\phi = \text{const}$.

Dans le cas considéré nous aurons:

$$X_x = -\frac{\pi}{2l} C \left\{ \frac{\operatorname{sh}\frac{\pi y}{l}}{\operatorname{ch}\frac{\pi y}{l} - \cos\frac{\pi x}{l}} - \frac{\pi}{2l} y \left[1 - \frac{\sin^2\frac{\pi x}{l} - \operatorname{sh}^2\frac{\pi y}{l}}{\left(\operatorname{ch}\frac{\pi y}{l} - \cos\frac{\pi x}{l}\right)^2} \right] \right\}; \quad (7)$$

$$Y_y = -\frac{\pi}{2l} C \left\{ \frac{\operatorname{sh}\frac{\pi y}{l}}{\operatorname{ch}\frac{\pi y}{l} - \cos\frac{\pi x}{l}} - \frac{\pi}{2l} y \left[1 + \frac{\sin^2\frac{\pi x}{l} - \operatorname{sh}^2\frac{\pi y}{l}}{\left(\operatorname{ch}\frac{\pi y}{l} - \cos\frac{\pi x}{l}\right)^2} \right] \right\}; \quad (8)$$

$$X_y = -\frac{\pi^2}{2l^2} C \frac{y \sin\frac{\pi x}{l} \operatorname{sh}\frac{\pi y}{l}}{\left(\operatorname{ch}\frac{\pi y}{l} - \cos\frac{\pi x}{l}\right)^2}. \quad (9)$$

Pour déterminer la constante C nous avons une condition évidente:

$$\int_{-l}^{+l} Y_y \, dx = -P,$$

P étant la force comprimante, appliquée au bord de la bande.

Cette condition nous donne:

$$C = \frac{P}{m}.$$

Les valeurs des pressions Y_y pour diverses sections transversales, calculées suivant la formule (8), sont indiquées dans la table 1.

Table 1

$x:l$ \ $y:l$	0.1	0.5	1.0	2.0
	$\frac{P}{2l}$	$\frac{P}{2l}$	$\frac{P}{2l}$	$\frac{P}{2l}$
0.	12.730	2.566	1.387	1.026
0.2	0.509	1.913	1.297	1.023
0.4	0.044	0.973	1.088	1.007
0.6	0.010	0.465	0.869	0.991
0.8	0.004	0.261	0.719	0.978
1.0	0.003	0.208	0.667	0.972

Les tensions X_x^0, produites par la force P, peuvent être déterminées par la formule suivante:

$$X_x^0 = X_x + \frac{P}{2l} \frac{\operatorname{sh}\frac{\pi y}{l} - \frac{\pi y}{l}\operatorname{ch}\frac{\pi y}{l}}{1+\operatorname{ch}\frac{\pi y}{l}}. \tag{10}$$

Les valeurs des tensions X_x^0 pour $x=0$ sont indiquées dans la table 2.

Table 2

$y:l$	0	0.1	0.5	1.0	2.0
X_x^0	0	$0.207\,\frac{P}{2l}$	$0.619\,\frac{P}{2l}$	$0.374\,\frac{P}{2l}$	$0.038\,\frac{P}{2l}$

Manuscrit reçu
le 11. II. 1938.

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Comptes Rendus (Doklady) de l'Academie des Sciences de l'URSS
1938. Volume XVIII, № 9

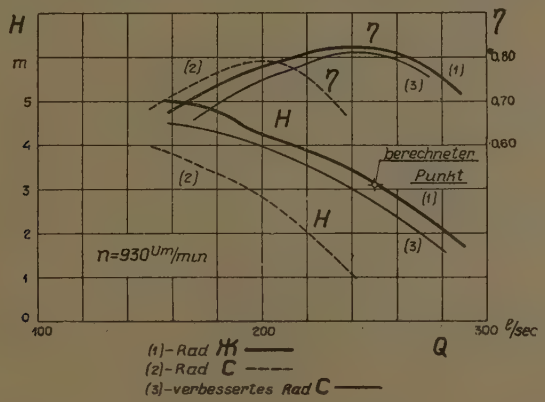
HYDRAULIK

VERGLEICH ZWEIER AXIALPUMPEN, VON WELCHEN DIE EINE NACH DER JOUKOWSKISCHEN THEORIE UND DIE ANDERE NACH DER THEORIE DER GESCHWINDIGKEITSDREIECKE BERECHNET SIND

Von P. A. WALTHER, korrespondierendem Mitglied der Akademie, und W. A. STEFANOWSKI

(Vorgelegt von S. A. Tschaplygin, Mitglied der Akademie, d. 14. II. 1938)

Es gilt überall für unrichtig, die Axialpumpen nach Geschwindigkeitsdreiecken zu projektieren (1), wie es vor 25 Jahren für alle hydraulische Räder gebrauchlich war. Man macht gegenwärtig die Berechnung entweder nach Tragflügeltheorie (1, 2, 3, 4), welche man gewöhnlich für Propeller anwendet, oder



man führt in die Geschwindigkeitsdreiecke irgendeine Korrektur [Uebertreibungswinkel (1) u. s. w.] ein.

Die Verfasser dieses Artikels—P. A. Walther und W. A. Stefanowski—hatten ein Rad der axialen Pumpe (Rad C) mit Hilfe der Geschwindigkeitsdreiecke konstruiert und prüften es zusammen mit einem anderen Rad (Rad $Ж$), welches nach der Joukowskischen Theorie (Tragflügeltheorie) berechnet wurde. Die Räder hatten die gleichen äusseren und inneren Durchmesser ($D = 350$ mm, $d = 160$ mm).

Die Ergebnisse der Prüfung der Räder bei $n = 930$ Um./min. sind auf der Figur gegeben. Da die beide Räder für einen Betriebszustand: $n = 930$

Um./min., $Q = 250$ l/sec., $H = 3.1$ m berechnet sind, so sind die Prüfungsergebnisse für das Rad $\mathcal{K}$, welches im optimalen Punkte der charakteristischen Kurven $Q = 243$ l/sec. und $H = 3.35$ m gibt, hinreichend gut. Dasselbe kann man nicht in bezug auf das Rad C wiederholen. Dieses Rad gibt in seinem besten Punkte $Q = 202$ l/sec., was sich sehr von der Rechnungswassermenge $Q = 250$ l/sec. unterscheidet. Die entsprechende Förderhöhe der Pumpe ist auch kleiner, als die berechnete. Auch gibt das Rad für $Q = 250$ l/sec., wo es nach der Berechnung $H = 3.1$ m haben sollte, nur $H = 0.9$ m (!!).

Der beste Wirkungsgrad des Rades C ($\eta = 0.793$) ist wieder kleiner als derselbe des Rades $\mathcal{K}$, welches $\eta = 0.82$ gegeben hat.

Nach all dem gesagten dürfen wir den folgenden Satz aufstellen:

Das axiale Rad von der grossen Umlaufzahl ($n_s = 730$), *in welchem die Schaufeln nach den Geschwindigkeitsdreiecken* (*ohne Anstellwinkel*) *gestellt sind, gibt nicht die volle berechnete Fördermenge und schafft eine kleinere Förderhöhe.*

Um die Eigenschafte, welche das Rad C gezeigt hat, zu verbessern, haben wir seine Schaufeln um den Winkel 4° gedreht, so dass sie in der relativen Strömung an einen positiven Anstellwinkel gestellt werden. Die Winkelgrösse haben wir aus einer Reihe von Versuchen bestimmt, so dass sie uns den möglichst besten Wirkungsgrad verschafft.

Die Kurven (*3*) zeigen, was aus dem Rade nach solcher Veränderung geworden ist. Wir sehen daraus, dass der beste Wirkungsgrad jetzt der Wassermenge $Q = 243$ l/sec. entspricht und $H = 2.92$ m gibt. All das unterscheidet sich nicht so sehr von den Rechnungsgrössen. Der beste Wirkungsgrad der Pumpe hat auch zugenommen und ist $\eta = 0.81$ geworden.

Wir dürfen also behaupten, dass unsere Versuche den folgenden Satz ergeben:

Wenn wir die Pumpenschaufeln, welche nach Geschwindigkeitsdreiecken profiliert sind, einen kleinen positiven Anstellwinkel in der relativen Strömung geben, so können wir die Fördermenge und Förderhöhe der Pumpe vergrössern, dadurch ihre Ergebnisse den Rechnungsgrössen nähern und gleichzeitig den Wirkungsgrad dieser Pumpe verbessern.

Dieses Resultat stimmt, augenscheinlich, mit den allgemeinen Sätzen der gegenwärtigen Hydromechanik sehr gut überein und seine Bedeutung liegt auch darin, dass es auf einem indirekten Wege diese Sätze bestätigt.

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Eingegangen
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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

PHYSICS

ON THE DISPERSION OF ELECTROMAGNETIC WAVES ABOVE THE EARTH'S SURFACE

By J. L. ALPERT, V. V. MIGULIN, P. A. RIASIN

(Communicated by S. I. Wavilow, Member of the Academy, 15. II. 1938)

1. Introduction

The dispersion of radiofrequency electromagnetic waves propagating along the earth's surface, judging from the literature on the subject, has not yet been thoroughly investigated. General * theoretical considerations allow us to draw some conclusions concerning this problem. Dispersion is to be expected, for instance, in case of propagation along dry land. On the other hand, when propagation of waves in the radiofrequency range takes place along the sea surface, dispersion should practically be absent.

A more exact knowledge of the laws governing the propagation of radiowaves under real conditions has become lately of practical importance in connection with the problem of measurung distances ([1]), in the first place above the sea surface. The same problems arise also in connection with other, for instance, ionospheric measurements ([2,3,4]).

Very little has been published up till now on propagation of radiowaves under real conditions. Moreover the results of these few works are conflicting. Thus, R. C. Colwell and his collaborators ([5]) have obtained for the velocity of radiowaves values of the order of 60 per cent of the velocity of light c, which contradicts the results of other investigators ([1,6]).

The study of propagation of radiowaves under real conditions, in which the decisive part at present belongs to the experiment, being of practical importance, experiments were undertaken with the aim to investigate directly the dispersion of radiowaves under real conditions, in the first place, along the sea surface.

Some results of the experimental investigation of the dispersion of medium radiowaves carried out by the Oscillation Laboratory of the Physical Institute of the Academy of Sciences of the USSR by the interference method proposed by L. I. Mandelstam, Member of the Academy, and N. D. Papalexi, Corresponding Member of the Academy, and using the apparatus devised and constructed in the Laboratory, are given below.

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* The works of Zenneck, Sommerfeld, Weyl, Fock, van der Pol and Niessen.

2. A Brief Description of the Method and Apparatus Used

If two coherent waves having frequencies ω and $m/n\ \omega$ (m/n being a rational number) and a definite phase difference φ_0 are radiated from point A, then in the absence of dispersion the same phase difference would be maintained at any point in the space. In the presence of dispersion, however, we should expect at point B at a distance r from A a different phase difference:

$$\Phi = \varphi_0 + \omega r \left(\frac{1}{v_1} - \frac{1}{v_2} \right) .$$

Here v_1 and v_2 are the phase velocities of both oscillations. It is also supposed that the geometrical paths of both waves coincide and that the difference in the optical path lengths which causes the additional phase to shift is due solely to the divergence of the values of the phase velocities v_1 and v_2.

Measuring Φ for different r's (φ_0 being maintained constant) and comparing the results obtained we are able to determine $\frac{1}{v_1} - \frac{1}{v_2}$.

The variations Φ are connected with the variations of r by the following relation:

$$\Delta\Phi = \omega \left(\frac{1}{v_1} - \frac{1}{v_2} \right) \Delta r,$$

wherefrom we obtain approximately:

$$\frac{\Delta v}{v} = \frac{\Delta\Phi \cdot c}{\omega \cdot \Delta r} .$$

(Here $v = \sqrt{v_1 \cdot v_2}$, and c may be substituted for v without affecting the accuracy of the measurements; moreover, according to the results of

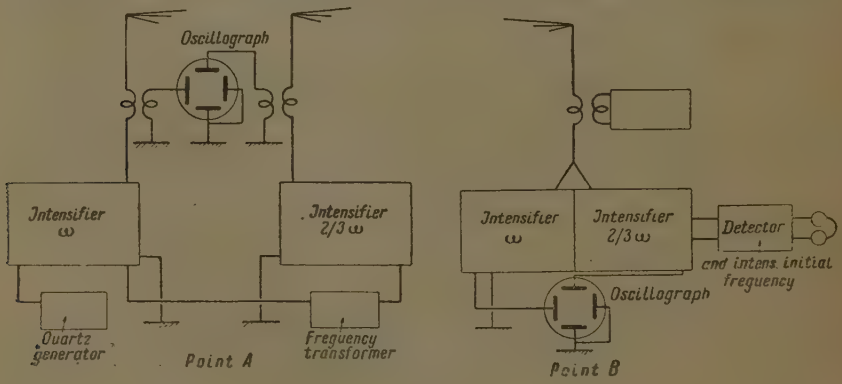

Fig. 1.

L. I. Mandelstam and N. D. Papalexi [1], those quantities are very close to one another.)

In order to carry out these measurements a dispersion radiointerferometer was constructed consisting of two low-power (10—15 Watt) transmitters incorporated in a common screening case (Fig. 1) and working at point A on two closely situated equal aerials. A piezo-quarz oscillator of frequency ω was used for frequency stabilization, one of the transmitters being synchronized on its fundamental frequency ω and the second through a frequency transformer which allowed to reduce ω to $^2/_3\ \omega$ and also to adjust a desirable phase difference of both radiated oscillations.

The phase difference of the oscillations radiated by both aerials was determined or controlled from the corresponding Lissajous figure on the screen of a cathode-ray oscillograph, whose two pairs of deflecting plates were coupled each with one of the aerials.

At point B a double receiver was working from a single aerial, in which the incoming waves induced oscillations of the frequencies ω and $^2/_3\,\omega$ and a definite phase difference corresponding to the given point. The received oscillations after having been amplified were led from the outputs of the receiver to the deflecting plates of a cathode-ray oscillograph giving on its screen a Lissajous figure, from which the phase difference of the oscillations at the outputs of the double receiver could be determined.

In order to exclude the phase displacement introduced by the receiver itself, a supplementary arrangement was used (a so-called «deviometer») which in the absence of incoming waves induced in the receiving aerial oscillations of the same frequencies and of a known constant phase difference. From the Lissajous figure obtained on the oscillograph screen from the deviometer the phase displacement introduced by the receiver * could be calculated (or maintained constant in each case).

3. Experiments Carried Out and Results Obtained

The final adjustment of the apparatus and the first experiments were carried out in the Moscow region near Zvenigorod.

Several measurements were carried out, r being equal to: 3.8 km, 7.3 km, 7.8 km, 13.6 km and 18.6 km. The frequency ω used was $2 \cdot 10^6$ rad/sec. which corresponds to a wavelength $\lambda_1 = 300$ m. The second wavelength was accordingly $\lambda_2 = 450$ m.

From these few experiments follows that for the given characteristic of the surface (meadows, tillage, woodlands) a dispersion of the order of a few tenths per cent is possible.

The fundamental experiments which confirmed the correctness of the conclusion on the absence of dispersion of electromagnetic waves propagating along a sea surface were carried out in the Kandalaksha gulf of the White Sea. Such surface (a free sea surface) possesses a considerable dielectric constant and a large conductivity and is uniform and smooth in the optical sense.

In these experiments the transmitting arrangement (point A) was on a ship (hydrographical ship «Papanin»**) and the receiver (point B) was placed on an island (Volostrov) close to the sea shore.

When the ship was moving, a continuous change of r occurred and, be a dispersion present, a continuous variation of the phase difference of the incoming waves (of the Lissajous figure) at the receiving point would have been observed. The deviometer was used only for controlling the constancy of the double receiver from the viewpoint of the constancy of its phase deviation.

Observations on a moving ship were carried out on August 9th, 11th, 15th and 17th, on October 28th and November 3d, 4th and 9th, Δr varying from 4 to 10 km.

These experiments have shown that within the limits of the precision of the apparatus for the above mentioned variations of the distance Δr bet-

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* It should be noted that the method of controlling the phase deviation mentioned here differs from that described in the paper of C. E. Viller (7) chiefly in that the mutual phase displacement of two oscillations passed through two channels (two receivers) is determined.

** The authors take the opportunity to express their gratitude to the staff of the expedition of the Hydrographical Administration of the North Sea Route and of the ship «Papanin» for their kind assistance in carrying out the here described experiments.

ween both points, no systematical variation of the phase difference at the receiving point was observed.

The numerical data obtained allow us to deduce that for the conditions mentioned here (propagation along a free sea surface) the possible dispersion $\Delta v/v$ is less than 0.07 per cent.

Several experiments were also carried out with the ship hidden behind land (cape Turii in the Kandalaksha gulf) which have shown that the appearance of land on the propagation path of radiowaves exerts a definite influence on the phase difference of the oscillations at the receiving point. The data obtained from these experiments do not allow however to draw conclusions on whether the cause of the phase variations observed were due to dispersion or to some other phenomena of a diffractional nature. It would be of interest to note that all the results could be brought into agreement with the numerical values obtained from Zenneck's approximate theory for ε and σ taken from the existing literature (for water $\varepsilon=80$; $\sigma>3\cdot10^8$, and for land $\varepsilon=5$, $\sigma\approx10^7$).

Conclusion

Based on the interference method proposed by L. I. Mandelstam and N. D. Papalexi, an apparatus for the investigation of the dispersion of radiowaves—a dispersion radio-interferometer—was devised in the Oscillation Laboratory of the Physical Institute of the Academy of Sciences.

Using this apparatus a series of experiments on the investigation of the dispersion of electromagnetic waves in the range $\lambda=300$—450 m propagating above a free sea surface were carried out in the Kandalaksha gulf of the White Sea.

The results obtained show that under these conditions the dispersion $\Delta v/v$ at any rate did not exceed 0.07 per cent.

For propagation over dry land under the conditions of the Moscow region as well as in the Kandalaksha gulf the preliminary experiments carried out indicated a possible dispersion (up to a few tenths per cent for the Moscow region).

Investigations in this direction are being prolonged in the Oscillation Laboratory of the Physical Institute of the Academy of Sciences under the leadership of prof. N. D. Papalexi, to whom the authors express their deep gratitude.

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Received
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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

PHYSICAL CHEMISTRY

INVESTIGATION OF THIN LAYERS OF ORGANIC SUBSTANCES AT THE MERCURYSOLUTION BOUNDARY BY THE METHOD OF CAPACITY MEASUREMENTS

I. HIGH-MOLECULAR ALCOHOLS AND ACIDS

By A. GORODEZKAYA and A. FRUMKIN, Member of the Academy

The examination of thin layers on the surface of mercury in solutions of electrolytes presents considerable interest since it affords the possibility of studying the influence of the electric field upon the properties of the layer. Moreover, at this boundary it is possible to obtain thin polylayers since, as it was shown in one of the foregoing papers (1), a drop of organic acid spreads completely over the surface of the mercury electrode polarized to the potential corresponding to the maximum of the electro-capillary curve. Yet, the application of the basic methods used in studies of monolayers on the surface of water to investigations of the boundary mercury/solution encounters greaf difficulties.

In the present paper we propose a new method for the study of thin layers at this boundary, based on the fact that the capacity of the double electrical layer of a metallic electrode, in the case of the penetration of organic molecules into that double layer, ought to be considerably reduced. In the case of soluble capillary-active organic substances this effect is well-known from measurements of electro-capillary curves and has of late found additional support in direct measurements of capacity (2). The method of capacity measurements made use of in the present work does not differ essentially from the method formerly developed by M. A. Proskurnin at this Institute (3).

All measurements were effected with a current of 50 Herz in norm. Na_2SO_4 acidulated by H_2SO_4 up to 0.001 norm. acidity*. The potential of mercury was measured against the reference electrode Hg/norm Na_2SO_4 saturated with Hg_2SO_4. For control of surface purity the capacity of the mercury electrode was always measured before the organic substance was applied.

The curves characterizing the dependence of the capacity of the clean mercury surface on cathodic polarization in norm. Na_2SO_4 are represented in all graphs by dotted lines.

The application of the organic substance was effected by means of the contact with the solid substance or else by pressing a drop out of a micropipette on the mercury surface polarized to the potential, corresponding

* In a neutral solution the fatty acid layers on mercury are unstable.

to the optimum spreading of the given substance over mercury. Palmitic acid dissolved in benzene was applied upon a surface which had not yet been covered with the solution of the electrolyte.

1. Measurements of Electrode Capacity with Constant Surface

Cetyl alcohol (Fig. 1). The film was produced by prolonged contact of the solid substance with the surface. The shape of the curve which gives the relation between capacity and polarization shows that the film is retained on the surface only within the interval 0.1—1.7 V; in the middle portion of the curve, between 0.6 and 1.1 V, the capacity is constant and equals 1.03 $\mu F/cm^2$.

Palmitic and oleic acids (Fig. 2 and 3) give curves differing from the curve for alcohol by the existence of a second horizontal part correspond-

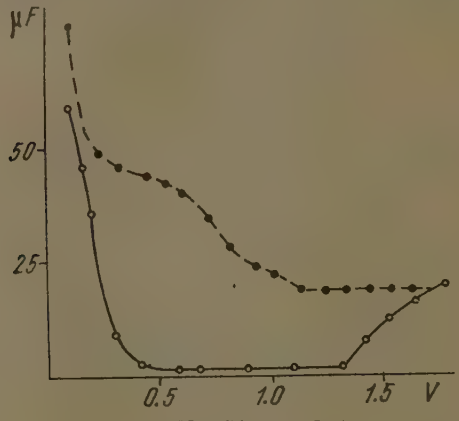

Fig. 1. Cetyl alcohol.

ing to ~5 $\mu F/cm^2$. The minimum capacity for a single monolayer of palmitic acid equals 2.4 $\mu F/cm^2$ and for 10 layers—0.80 $\mu F/cm^2$*; while even after 2 or 3 hours of «rubbing» the surface with a crystal, the capacity failed to drop below 3.5 $\mu F/cm^2$.

The minimum capacity for a thickness equal to 0.8 of a monolayer of oleic acid equals 5 $\mu F/cm^2$ while it reaches 0.32 $\mu F/cm^2$ for 8 monolayers.

Sharp maxima for potential values corresponding to the limits of stability of the film are clearly to be seen on the capacity curves of fatty acids. The reason for the appearance of these maxima was explained formerly; the theory thereof will be examined more elaborately in another paper.

A number of experiments were also carried out with a large amount of oleic acid (50—1000 monolayers). [The oleic acid, of «Kahlbaum» grade, was not subjected to further purification. It is certain that the preparation was not sufficiently pure.] With such quantities, and when observations are made at a small angle to the surface, interference colours can be observed

* Under the term «monolayer» we understand an amount of organic matter which corresponds to an area of 20.5Å² per molecule.

on the mercury at polarization corresponding to the maximum spreading, the colour of the surface varying with the potential.

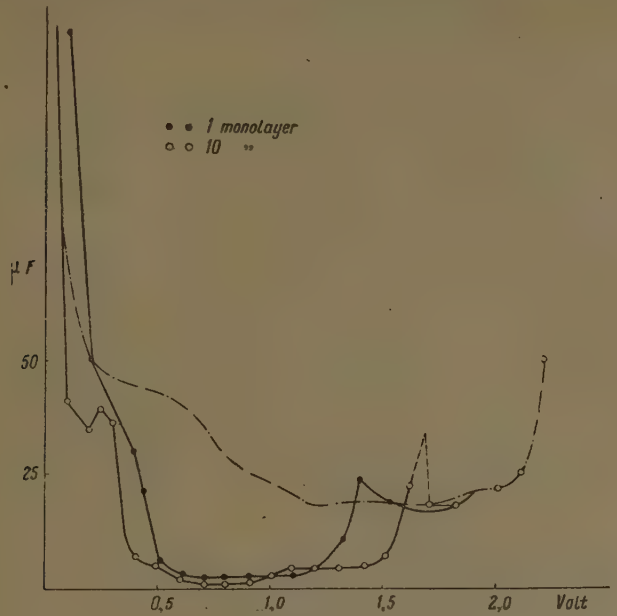

Fig. 2. Palmitic acid.

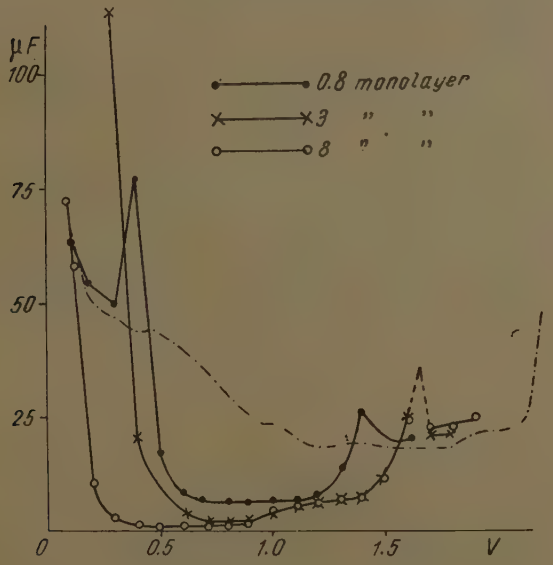

Fig. 3. Oleic acid.

As polarization recedes from values corresponding to the region of maximum spreading, the film breaks up into separate coloured spots whose edges have sometimes a colour differing from that observed in the middle.

With further change of polarization the spots coalesce into colourless lenses and finally into spherical drops, as was already described previously[1].

In order to clear the question of the equilibrium of such polylayers, experiments were carried out with gradual application of the acids.

Measurements of Capacity with Gradual Application of Oleic Acid. Polarization 0.75 V

Number of monolayers of acid	Capacity in μF/cm²	Colouring of mercury surface
1.25	1.16	Not coloured
4	1.16	» »
7	1.21	» »
13	1.15	Small faintly coloured spots
18.5	1.15	Fairly well visible red spots
25	1.19	Spots brighter and larger
43.5	1.08—1.18	Spots coalesce to form network
43.5 vessel heated to 60°	1.84	Red and green spots
43.5 vessel cooled to 20°	1.55	» » » »
68.5	0.71	Whole surface red
117	0.30	» » »

The curve taken with a film of 117 layers fully coincided with the curve for 8 layers when these have been applied at once (Fig. 3).

It will be seen that with the gradual application of the acid, the capacity reaches a certain limiting value, provided the amount slightly exceeds a monolayer. The excess of the acid remains in the form of spots in equilibrium with the monolayer and affects but little the magnitude of the capacity. This continues till, with about 60 layers, the spot covers almost the whole surface, when a new reduction of capacity takes place. As can be readily seen from the values of capacity given in Fig. 3, practically continuous polylayers are obtainable from a much smaller amount of the substance, provided the substance be applied at once. However, even though these layers may exist for several hours, they are not in equilibrium and when kept for a long time spots appear on them, the capacity increasing simultaneously. At the same time polylayers of a thickness of 50—100 molecules are apparently quite stable. It is interesting to note that in the case of oleic acid at the boundary mercury/solution—notwithstanding the absence of a measurable angle of contact—within a certain interval of the layer thickness the layers are unstable.

2. Experiments with Compression of the Mercury Surface

In these experiments the mercury was placed in a conical funnel and the change of the surface was effected by lifting or lowering the mercury level.

In the case of cetyl alcohol, the capacity of the layer at first decreased somewhat under the action of compression and then assumed a constant value in the neighbourhood of 0.91 μF/cm².

Palmitic and particularly myristic acids yield under compression polylayers with lower values for the capacity; thus, with a threefold diminution of the surface, the capacity of the layer of myristic acid falls down from 1.26 to 0.46 μF/cm². Yet these polylayers are unstable and their capacity increases with time.

Calculation of Layer Thickness

Our measurements afford the possibility of calculating the effective thickness of a layer d from its capacity C, according to the formula for surface condensers: $C = \frac{\varepsilon}{4\pi d}$, where ε is the dielectric constant. In this case it will obviously be necessary to take for ε a value which would be free from the dipole effect (in the adsorbed layer the dipoles are certainly oriented and have lost their freedom of rotation); e. g. in the case of cetyl alcohol ε calculated from the index of refraction or from the sum of polarizabilities of all bonds in the molecule equals 2.07. Moreover, in order to obtain a value of C which would equal $\frac{\varepsilon}{4\pi d}$, it will be necessary to introduce a correction for the capacity of the ionic layer C_2 into the observed value of capacity C_1, using the formula $\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$, since the whole system may be considered as two condensers in series. However, as the value C_2, known from measurements taken with a clean mercury surface, equals 20—30 $\mu F/cm^2$, i. e. by far surpasses C_1, the respective correction is very small. The following values of d were obtained:

A layer of cetyl alcohol under maximum compression, $d = 1.9 \cdot 10^{-7}$.

A layer of oleic acid in equilibrium with polylayers, $d = 1.5 \cdot 10^{-7}$.

The value for cetyl alcohol is fairly close to the length of the molecule determined by other methods, e. g. from the amount of matter in a condensed layer on the free surface of water; the value for oleic acid lies lower. It should, however, be borne in mind that in the case of even a partial penetration of the solution of the electrolyte between the molecules of a monolayer, the effective thickness of the monolayer as calculated from capacity measurements will be much lower than its true value. In this way capacity measurements provide a sensitive criterion for investigating the structure of these layers.

At present an apparatus is being designed by us which will permit to carry out measurements of capacity at different values of the area per molecule.

In the case of polylayers calculations of the thickness from capacity afford quite reasonable results until the thickness of the layer does not exceed 2 to 3 monolayers. For thicker layers too low values are obtained. This is, however, just the thing to be expected, since, in case of sufficiently thick layers, our method of measurement should give no longer the thickness of the layer of the organic substance, but the thickness of a diffuse double layer, produced by the ions of the electrolyte penetrating into the layer of the organic substance from the water phase, at least at such frequencies of alternating current, at which the equilibrium distribution of ions has time to become established.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
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CHEMISTRY

ON COMPOUNDS OF PLATINUM AND CARBON MONOXIDE

By ANNA GELMAN and M. BAUMAN

(Communicated by N. S. Kurnakoff, Member of the Academy, 10. II. 1938)

Compounds of platinum and carbon monoxide were obtained for the first time by Schützenberger (1) in 1868, by passing a stream of chlorine and carbon monoxide over a platinum sponge, heated to 250°. We succeeded in producing the following compounds: $PtCl_2CO$; $PtCl_2.2CO$ and $2PtCl_23CO$. We also obtained $PtCl_2.CO.2NH_3$; $PtCl_2.2CO.2NH_3$; $PtClCOC_2H_3$ by passing ammonia and ethylene carbon tetrachloride solutions of these compounds.

In 1891 Pullinger (2) synthesized the compound $PtCl_22COCl$ from Pt, CO and Cl_2 and while attempting to synthesize this compound from $PtCl_4$ and CO, he produced: $PtCl_2.CO$; $PtCl_2.2CO$ and $2PtCl_2.3CO$. He also obtained $PtBr_2CO$.

In the same year (1891) Mylius and Foerster (3) obtained large quantities of a salt of the Zeise type, viz.: $aH[PtCOCl_3]$, where $a=C_5H_5N, C_9H_7N$ etc. and also $CoPtx_2$, where $x=Cl'$; Br'; J'.

Foerster (4) further studied some of these compounds and synthesized a number of new ones.

Schützenberger's investigations were confirmed by Manschot (5) in 1925.

We took interest in the compounds of platinum and carbon monoxide under the hypothesis that carbon monoxide, being an unsaturated molecule, should behave in the complex analogously to ethylene. Unfortunately, among the works of the authors mentioned above we did not find anything from which we could draw any conclusions as to the trans-activity of carbon monoxide, and so we decided to make an investigation of the compounds of platinum and CO.

These compounds were obtained in the same manner as the ethylene aminochlorides of platinum (6), i. e. a solution of potassium or ammonium chloroplatinate was kept under the action of carbon monoxide for 7—14 days at room temperature. We followed the course of the reaction by the colour of the solution, which gradually turned yellow, and by the insignificant quantities of platinum liberated. Besides this a dark cherry-red film (containing platinum) formed on the surface of the solution. This film is insoluble in HCl, but dissolves in nitric acid generating a gas. (A more detailed study of this substance will be made in the future.)

When an aqueous solution of pyridine (Py) was added drop by drop to the greenish-yellow filtrate, which probably has the composition $K[PtCOCl_3]$, there at once appeared a yellow precipitate. The reaction took place according to the equation:

$$Me[PtCOCl_3] + Py \rightarrow \downarrow [PtCOPyCl_2] + MeCl.$$

The precipitation with pyridine was conducted in small portions and the solution was constantly cooled with ice water, but although we took every precaution, we rarely succeeded in obtaining the substance absolutely pure right away; we generally found it neccessary to reprecipitate it from a hydrochloric acid solution. We did not succeed at all in producing the pure substance with ammonia.

The yellow precipitate was washed several times with absolute ether and dried over P_2O_5.

Analyses of this substance showed without further doubt that its formula is $PtCOPyCl_2$.

While determining the chlorine content of this compound we came across an interesting fact, viz.: if a sample of this substance is decomposed with hot water and then $AgNO_3$ is added to the filtrate, only $^2/_3$ of the chlorine (12.73%; 12.17%; 12.79%) is precipitated. About the same amount of chlorine precipitates after the solution has been reduced with zinc.

Even after it had been intensely heated with soda in a platinum crucible, the percentage of chlorine rose only to 13.57%. Results approaching the theoretical ones were obtained only when the substance was reduced slowly with magnesium in acetate solution (17.41%) (theoretical result—19.02%).

$PtCOPyCl_2$ was reproduced up to ten times. The reactions took place without fail in all cases, but the amount of substance produced was not large, viz.: from 2.5 g $(NH_4)_2PtCl_4$, 0.76 g $PtCOPyCl_2$ was produced (theoretically 2.5 g), which is only 30.40% of what it should be according to theory.

Properties of $PtCOPyCl_2$

$PtCOPyCl_2$ is lemon-yellow in colour and forms tiny crystals; water decomposes it slowly in the cold, but very quickly when heated. Obviously the following reaction takes place

$$[PtCOPyCl_2] + H_2O = Pt + CO_2 + Py + 2HCl.$$

In this reaction a by-product is formed which keeps back $^1/_3$ of the chlorine in the compound.

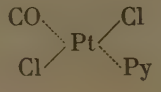
The solubility of $[PtCOPyCl_2]$ in C_2H_5OH at 25° C is 0.069 g in 100 cm^3 solution. When heated in air in a capillary tube the substance melts and then at 127—129° C begins to decompose quickly.

$PtCOPyCl_2$ dissolves readily in dilute hydrochloric acid. When the solution is evaporated lustrous gold-yellow crystals are formed. These crystals have the composition $PyH[PtCOCl_3]$ and are identical to those described by Mylius and Foerster (l. c.). Similarly to lunar caustic the solution of this salt gives black spots on the skin and on cloth, hardly to be blotted out. When pyridine is added, the initial substance ($PtCOPyCl_2$) immediately precipitates.

Consequently compounds of platinum and CO show the same remarkable equilibrium as was first observed in the ethylene compounds by Černyaev [6] in collaboration with one of us, viz.:

$$[PtCOPyCl_2] + \underset{Py+}{\overset{HCl}{\rightleftarrows}} PyH[PtCOCl_3],$$

and which again can be explained only by the great trans-influence of carbon monoxide. In analogy with the ethylene compounds, $PtCOPyCl_2$ may be given the following trans-form:



The formation of the respective cis-isomer when a solution of Koss' salt is treated with carbon monoxide proves that the ethylene and carbonyl compounds of platinum are perfectly analogous to each other.

Koss' pyridine salt gave us too small a quantity of the substance for investigation. But with Koss' ammonium salt beautiful pale-yellow crystals crystallized out after 6—10 days according to the equation which we expected, viz.:

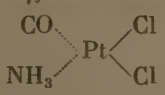
$$NH_4[PtNH_3Cl_3] + CO \rightarrow NH_4Cl + \downarrow [PtNH_3ClCOCl].$$

The latter reaction is very capricious; first of all, if the crystallic precipitate is not separated from the filtrate on time the products of reduction will make it impure; secondly, the reaction is very sensitive to temperature—normally it takes place only within the limits of 11—13°C.

When the temperature is raised to 20°C the dark cherry-red amorphous precipitate, mentioned above, is formed instead of the crystals. When cooled with ice the solutions did not give any reaction at all.

In the experiments good results were obtained only in four cases out of eight. Analysis fully confirms the supposed composition of the salt: ($PtNH_3$ ClCOCl); after filtration the salt was washed with absolute ether and dried in a desiccator over P_2O_5.

In this case it was not difficult to determine the quantity of chlorine. This compound, which, according to the conditions of its production ([7]), has the cis-form:



differs sharply on properties from the former. Thus, for instance, when heated in a capillary tube, it begins to decompose without melting only at 180—185°; water decomposes it instantaneously in the cold; its solubility in alcohol is 0.023 g in 100 cm^3 solution. It is insoluble in hydrochloric acid. After it had been decomposed with hot water, all the chlorine in the filtrate can be precipitated with lunar caustic. This salt is very similar in appearance to $[PtC_2H_4ClNH_3Cl]$.

While synthesizing and studying the carbonyl-aminodichlorides of platinum there are many difficulties to overcome, since these compounds are even less stable than the ethylene ones (only hydrochloric acid keeps them from decomposing). Besides this, as has already been mentioned, the temperature limits within which some of them can be obtained are too narrow.

Those data which we have, however, are enough to make it quite evident that we again have to do with space isomerism due to great trans-influence of CO. If the Py in the complex is replaced by ammonia, the difference in the properties of compounds of this type is not as pronounced as that observed formerly ([7,8]).

The high trans-activities of ethylene, its homologues and carbon monoxide in the complexes cannot be understood if we approach the question only from the point of view of the dipole hypothesis, since the polarizability of such molecules, not to speak of constant dipolar moments, is not great enough to make innerspheric activity possible.

Strictly speaking, such a phenomenon has already been observed in the nitro-compounds of platinum, which were studied in detail by I. I. Černyaev ([9]). According to data given by the author and confirmed also by other investigators, the nitro-group has a high trans-influence in comparison with the ions of the halogens. According to A. A. Greenberg's calculations (report delivered at the meeting of the Academy of Sciences) the nitro-group

Property	Cis-form	Trans-form
Colour	Pale-yellow	Pale-yellow
Solubility on C_2H_5OH at 25°C	0.023 g in 100 cm³	0.067 g in 100 cm³
Relation to H_2O in the cold	Decomposes at once	Decomposes gradually
Relation to H_2O when heated	Decomposes. Lunar caustic precipitates all the chlorid in the filtrate	Decomposes. Lunar caustic precipitates $^2/_3$ of the chlorine
Relation of the dry substance to heat	Decomposes without melting at 180—185°C	Melts and decomposes at 127—129°C
Relation to HCl in the cold	Does not dissolve	Dissolves, forming PyH [$PtCOCl_3$]

should not be so active judging by the magnitude of its polarizability. The author himself is perplexed by this circumstance, since he has calculated the polarizability of a whole series of substitutes and in all other cases found that the theory is confirmed in practice.

It seems to us that the high trans-influence of ethylene hydrocarbons, carbon monoxide and the nitro-group is due to the unsaturated state of the carbon and nitrogen atoms.

According to literary data ([10]) saturated hydrocarbons do not give complex compounds; on the other hand, it is well known that ammonia, similarly to the NO_3' ion, does not show any trans-influence in the complex, since the nitrogen atom in them has a stable electronic configuration.

Besides the nitro-group, among nitrogen compounds, according to our point of view, nitric oxide, NO, may also be expected to have a high trans-influence. At any rate in his review A. A. Blanchard ([11]) (1934) describes a large number of complex compounds of NO, drawing a complete analogy between them and carbonyl compounds.

It is apparently the homeopolar nature of the bound between unsaturated molecules and the nucleus atom that in the end conditions the effect of trans-influence.

Conclusions. 1. It has been established that CO, just as C_2H_4 and its homologues, has a high trans-influence in the complex.

2. On this basis carbonyl-aminodichlorides of platinum, having a composition of ($PtaCOCl_2$) in the cis- and trans-form, have been obtained after a method suggested before by one of us.

3. An attempt has been made to explain the high trans-influence of CO and also the trans-influence of C_2H_4 and NO'_3 through the fact that the atoms of carbon and nitrogen are unsaturated.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

CHEMISTRY

THE TRANSMITTING MECHANISMS OF ORGANIC REACTIONS

By E. A. ŠILOV

(Communicated by A. N. Frumkin, Member of the Academy, 21. II. 1938)

The recent investigations have extremely advanced the theory of the mechanism of the addition to double bond. It has been established that these reactions do never proceed by the way, which appeared formerly to be self evident and only possible. The addition does namely never develop as a simple bimolecular reaction, but it needs the participation of a third molecule. The rôle of the partner can be executed by an added or accidentally present catalyst or by the molecules of the solvent or of the walls of the vessel.

The addition mechanism is particularly evident in the case of a consecutive reaction, as it is, for instance, the addition of hypochlorous acid to ethylene. This reaction obeys the kinetic law (1):

$$-\frac{d[C_2H_4]}{dt} = l[HOCl]^2 = l_1 K[Cl_2O],$$

where K is the constant of the equilibrium $2\,HOCl \rightleftharpoons Cl_2O + H_2O$.

The slowest stadium of the reaction is evidently the formation of chlorine oxide, while the addition of ethylene proceeds relatively much faster. As the product of the reaction is 2-chloroethanol, but not the ester of hypochlorous acid, one must admit the participation of a water molecule in the reaction. Thus, the course of the addition must by represented by the scheme:

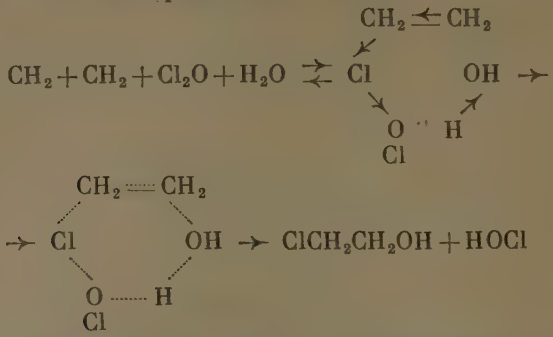
$$C_2H_4 + Cl_2O + H_2O \rightarrow \begin{matrix} H_2C & CH_2 \\ \diagup & \diagdown \\ Cl & \quad OH \\ O & \cdots H \\ Cl & \end{matrix} \rightarrow ClCH_2CH_2OH + HOCl.$$

According to the principles established by the «English school» of chemists (2) one must give to the last scheme the interpretation as follows *.

The active chlorine oxide molecule polarizes the ethylene molecule and adds to its negative end. The ends of the new polar system attract

* Besides certain details, my views differ from the statements of the English school, first, by my assumption of a much larger importance and wide-spreading of cyclic critical complexes, and secondly, by a more wide applying of the new ideas as do the English chemists.

the water molecule, closing the ring of a «critical complex», which dissociates then in stable compounds.



The arrows indicate the transfer or the displacement of the electrons.

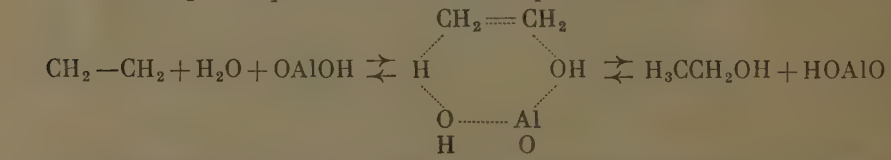
The analogous mechanism takes place in the addition to ethylenic bond of chlorine (3), bromine (4) and of the hypobromous esters (5).

The principle of the described mechanism can be applied to other reactions of addition and separation. Thus arises a hypothesis, which leads to very simple and convincing schemes of the course of the organic reactions.

I shall consider, as an example, the reaction of the dehydration of ethanol and the reverse reaction of the hydration of ethylene.

As known, these reactions can proceed only in the presence of many specific catalysts. I take alumina as a typical dehydrating catalyst and give him the formula OALOH *.

By analogy with the addition of chlorine oxide to ethylene we obtain the following conception of the chemical process:



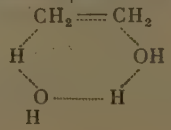
The critical complex is common one for the dehydration of alcohol and the hydration of ethylene.

The electron-dynamic picture of the process should be represented as follows.

The ethanol molecule cannot separate the water molecule. It is prevented, first, by the stereochemical conditions of the Van't Hoff tetrahedron, and secondly—in the much larger degree—by the necessity of a high polarization or, in other words, of a considerable activation of the molecule **.

* It is known that calcined alumina has no catalytic action. Therefore a certain degree of hydratation of alumina must be assumed. On other hand, the aluminium atom is in the form of OAlOH coordinately unsaturated to a greatest extent. This explains the choice of the formula of the active form of the catalyst.

** If only the steric conditions would be of importance, each polar substance, having some affinity to hydroxyl, for instance, hydrogen chloride or water, could catalyse the reaction, since it could form the critical complex as shown next. But such substances can cause the decomposition only of very labil compounds, e. g. HCl at triarylethanols.

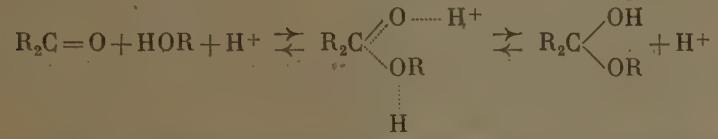


The rôle of the catalyst begins in the manner that the coordinately unsaturated, having an electron sextet, aluminium atom wants to seize the hydroxyl group of ethanol. In consequence his own hydroxyl group polarizes and connects with the opposite polarized hydrogen atom in the methyl group of ethanol molecule, closing the ring of the critical complex *, which then dissociates stable compounds.

The presented ideas have some common traits with the multiplet theory ([6]), at least with the part of it which deals with the mechanism of catalytic action. In particular, the postulate of the multiplet theory that the catalyst acts by two points is often (but not always) justified in our mechanisms. In both hypotheses one scheme applies to the direct and reverse reactions. The new hypothesis indicates, however, the rôle and the place of each atom of all partners of the reaction, what does not the multiplet theory. It brings at the same time the new idea that the reacting molecules exchange certain atoms with the catalyst.

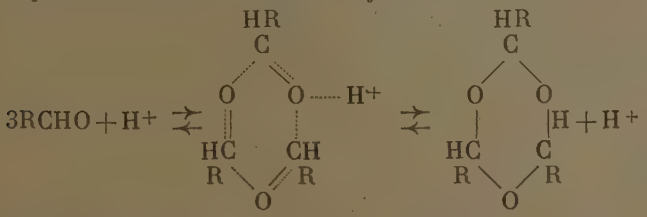
I give further the mechanisms of some typical organic reactions without proving them from chemical and kinetic side. For the simplifications of the schemes I do not show also the electronic perturbances in the reactions.

1. The Formation and Dissociation of Oxyethers



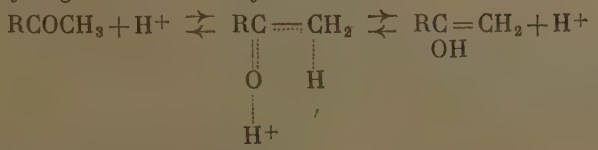
The formation and hydrolysis of esters proceeds in analogous manner through the intermediate form of a ortho-ester.

2. Polymerization of Aldehyds

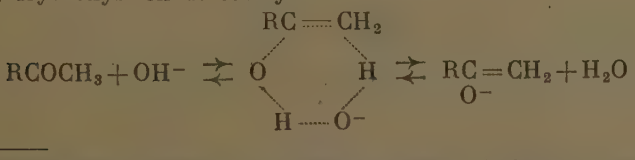


3. The Keto-Enolic Tautomerism

a) Hydrogen ion as catalyst:

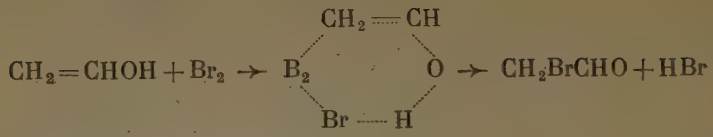


b) Hydroxyl ion as catalyst:

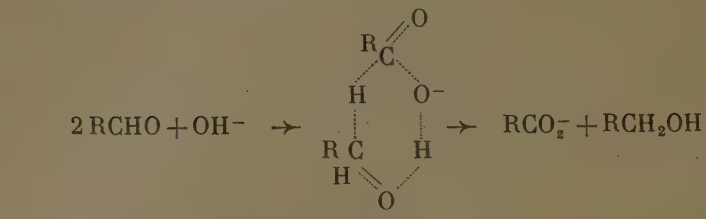


* Analogous rings appear in many other reactions. It is, however, prevailing but not obligatory condition of a transmitting mechanism. The ring form can be absent if the critical complex is composed by ions (see examples below).

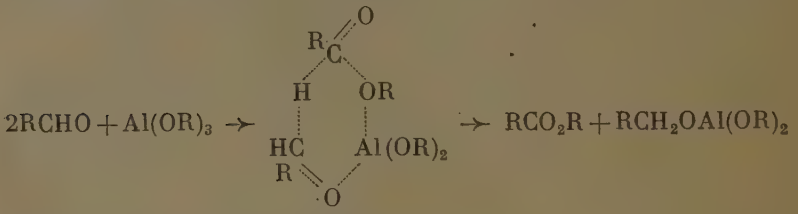
4. Bromination of an Enol



5. The Cannizaro Reaction



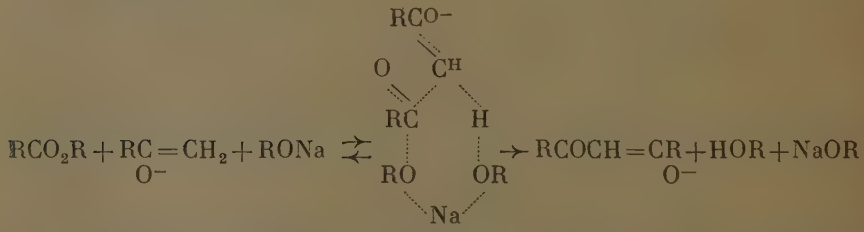
6. The Tishchenko Reaction



7. The Claisen Condensation*

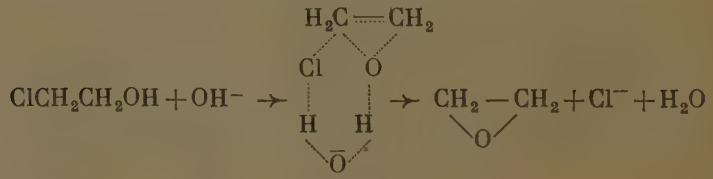
The first stadium is enolisation:

The second stadium:



The reaction can proceed through the enol form of an ester, if the given ester enolizes easier than the ketone.

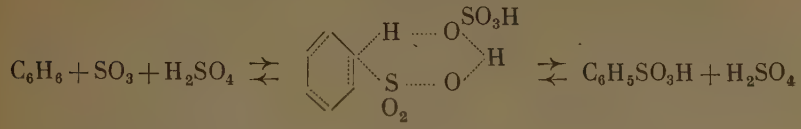
8. The Formation of an Oxyde



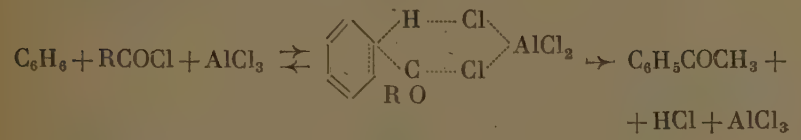
* The proposed mechanism of the Claisen condensation is much nearer to the considerations of Arndt and Eistert [6], as to hypotheses of W. Hückel [7] and G. W. Čelinzev [8].

9. The Substitutions in the Benzene Ring

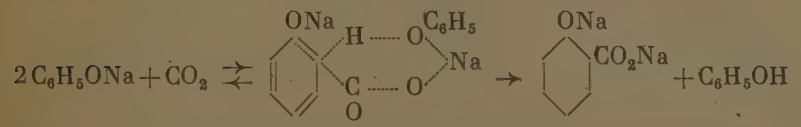
a) The sulphonation and hydrolysis of the sulphonic acids:



b) The Friedel-Crafts reaction:



c) The Kolbe synthesis of salycylic acid:



In analogous manner may be constructed the schemes of mechanisms of many other reactions. One must, however, have in view that the certain reactions can proceed through many consecutive stadiums. In this case the structure of the critical complex must be naturally considered separately for every stadium.

The hypothesis does not concern all organic transformations. In many cases the organic reactions proceed by other ways, particularly by ionic and chain mechanisms.

The considered examples suffice, however, I believe, for conclusion that the main part of organic reactions falls under the action of the principles exposed in this communication.

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Received
10. II. 1938.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

ANALYTIC CHEMISTRY

THE QUANTITATIVE SEPARATION OF NIOBIUM AND TITANIUM

By V. S. BYKOVA

(Communicated by V. I. Vernadsky, Member of the Academy, 7.II. 1938)

The most accurate method at present of separating the earthy acids ($Ta_2O_5+Nb_2O_5$) is Schoeller's «oxalate-salicylate» method (1). The Schoeller's method, although complicated, is, unfortunately, for the time being the only one of great accuracy.

Literature states that the separation of the earthy acids and titanium is one of the most difficult processes in mineral analysis. The Laboratory of Geochemistry of the Kola base of the Academy of Sciences came to the same conclusion while analysing some new minerals containing niobium (2). The predominance of titanium and the extremely small content of tantalum in the minerals made the task all the more complicated.

After it had been found that niobium was extensively spread in minerals of the Kola Peninsula, which were acquiring importance in industry and science, the Kola base endeavoured the working out of a method to determine it quantitatively. The first result was V. S. Bykova's work (3), in which a method of determining small quantities of earthy acids in loparite rocks was described. In this method use was made of Schoeller's «pyrosulphate-tannine» reaction, but instead of sulphuric acid, hydrochloric acid went into the composition of the reagent. Further investigation showed that our method could be used only when small quantities of earthy acids had to be separated, and the pentoxides did not have to be separated afterwards into tantalum and niobium. This method is applicable to such minerals as sphen, ramsaite, astrophyllite etc., which contain small quantities of earthy acids (4). But it fails in the case of minerals rich in earthy acids, such as loparite, fersmanite and murmanite, and also when the pentoxides produced have to be further separated into tantalum and niobium. The abundant tannine precipitates of the earthy acids are difficult to free from titanium. The results of separating niobium and titanium after our pyrosulphate-tannine method are given in Table 1. The bisulphate fusion of the oxide mixture was lixiviated by heating 200 cm^3 of the tannine reagent (1 g tannine+10 cm^3 HCl+90 $cm^3 H_2O$). The niobium tannine precipitate was filtered, washed and ignited, this treatment being performed many times. The weights *a* of the precipitates after a three times treatment are given in column 3. The quantity of titanium, which had been determined colorimetrically, was subtracted from *a*, and from the difference the quantity of Nb_2O_5 produced was established (column 5). The difference between the quantities of Nb_2O_5 taken and produced (i. e. the loss due to the process of separation from titanium) is given in column 6.

Table 1

No	Taken		a, g	TiO_2 in a, g	Nb_2O_5 produced, g	Loss in Nb_2O_5, g
	Nb_2O_5, g	TiO_2, g				
1	0.0515	0.2500	0.0540	0.0055	0.0485	0.0030
2	0.0510	0.2500	0.0530	0.0046	0.0484	0.0026
3	0.0508	0.2500	0.0530	0.0050	0.0480	0.0028

The results of the experiments show that: 1) The method is available in many cases and gives accurate enough results, if the loss of earthy acids, which varies according to the quantities of the reagent used(4), is taken into account. 2) The large quantity of titanium (column 4) in the niobium precipitates (a) shows that the pyrosulphate-tannine treatment is inadequate for large quantities of earthy acids to be determined, and that it fails completely when a subsequent separation of pentoxides of Ta and Nb is needed.

When determining Ta and Nb separately, the mixture of pentoxides must be freed from titanium to minimal quantities of the latter (5) before the pentoxides are separated. When small quantities of Ta are present, the test-portion should be as great as possible. These conditions are not to be fulfilled together with the pyrosulphate-tannine method. While looking for a simple and complete method of separating the earthy acids and titanium, we came upon the following reaction. When the fluorides of the earthy acids and titanium are dissolved in an acid solution of tannine (1 g tannine+10 cm^3 HCl+ +90 cm^3 H_2O), a rather stable, transparent solution is obtained. When boric acid is added, a tannine precipitate of the earthy acids falls out, while titanium stays in solution. With the help of this reaction it is possible to separate the elements mentioned more quickly than in any other way. Thus, for instance, when 50—100 mg Nb_2O_5 are separated from 200—250 mg TiO_2, less than 1 mg of titanium is left in the niobium precipitate after a threefold treatment, and about 4—7 mg Nb_2O_5 stay in the filtrate together with the titanium. We used the pyrosulphate-tannine method in extracting the rest of the niobium, altering it so as shorten the operation. By combining the fluoride-tannine and the pyrosulphate-tannine operations, which in themselves are very simple, it was found possible to separate the earthy acids and titanium with as great accuracy as Schoeller's best oxalate-salicylate method gives.

The operation. The whole quantity of oxide (0.3) is dissolved in 2—3 cm^3 HF in a covered platinum crucible and is heated in a water-bath. After heating, as much of the HF excess as possible is removed. The transparent syrup-like mass of fluorides is washed out with the reagent (100—200 cm^3) into a beaker. Boric acid is added (4—5 g to 100 cm^3 reagent); after this the solution is boiled about five minutes, and then is left in the cold for a few hours. The precipitate is filtered, washed with the same reagent diluted 1:2 with water, and ignited. This operation is repeated twice. Previous to ignition, the precipitate may be washed back into the beaker with the reagent (100 cm^3), boiled, and when cool passed through the same filter. This is generally superfluous, since the boric acid is completely washed away the first time. If titanium is present in large quantities, quite a lot of HF goes into compound; therefore in the first treatment of the fluorides it is necessary to reduce the acidity of the reagent by half, i. e. 5 cm^3 of HCl in 100 cm^3

of reagent. For the next treatment a reagent is taken of the composition given above, i. e. 1 g tannine+10 cm^3 HCl+90 $cm^3 H_2O$. The volume of the reagent for these reactions is 100—150 cm^3 to 50—100 mg Nb_2O_5.

The extraction of the rest of the niobium. All the filtrates are poured together; then they are evaporated to 400 cm^3 and neutralized with ammonia. 10—15 g ammonia acetate and 2—3 g tannine are added. The full volume now is 500 cm^3. When cool, it is passed through Buchner's filter and is washed with 2% NH_4Cl and a small quantity of tannine. When cool, the precipitate is transported to a beaker, where the reagent (1 g tannine+10 cm^3 HCl+90 $cm^3 H_2O$) is added (35 cm^3 to every 1 g TiO_2), and then it is boiled about 10—15 minutes. It is left to stand overnight and then it is filtered. After being ignited the precipitate is purified from titanium after our pyrosulphate-tannine method ([2]). At the end it is dissolved in HF+ $+H_2SO_4$ instead of being fused with $K_2S_2O_7$. The final little precipitate is ignited together with the main earthy acid precipitate; the full weight is *a*.

Table 2, given below, shows the results of separating after the method in question. The experiments were conducted mainly with Nb, since Ta is merely an insignificant admixture in the minerals of our region, and shows its influence only by improving results. The ratios of Nb_2O_5 and TiO_2 taken, are within the limits characteristic of the most important minerals.

Table 2

No	Taken		*a*, g	TiO_2 in *a*, g (color.)	Nb_2O_5 produced, g	Loss in Nb_2O_5, g
	Nb_2O_5, g	TiO_2, g				
1	0.0510	0.2500	0.0502	0.0010	0.0492	0.0018
2	0.0508	0.2500	0.0502	0.0010	0.0492	0.0016
3	0.0999	0.2000	0.0984	0.0014	0.0970	0.0029
4	0.1010	0.2000	0.0998	0.0017	0.0981	0.0029
5	0.1006	0.2000	0.0997	0.0017	0.0980	0.0026

In column 5 of this table we give the quantity of Nb_2O_5 produced, after subtracting TiO_2 (column 4) from the weight of the ignited final precipitate. The differences in the quantities of Nb_2O_5 taken and produced (column 1 and 5), which show the quantity of niobium lost in its separation from titanium, are given in column 6. These latter figures show that the values produced are 2—4 mg less than the true values. The use of Schoeller's oxalate-salicylate method in separating niobium and titanium gives a loss of the same order. The more or less constant limits of the error, which is always negative, make it possible to use an empiric correction, the value of which is determined from the figures in column 6 (Table 2).

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Received
11. II. 1938.

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Comptes Rendus (Doklady) de l'Academie des Sciences de l'URSS
1938. Volume XVIII, № 9

BIOCHEMISTRY

GLUCURONIC ACID AS AN INTERMEDIATE PHASE IN THE BIOCHEMICAL FORMATION OF CITRIC ACID FROM SUGAR

By V. S. BUTKEWITSCH, Corresponding Member of the Academy, E. V. MENZHINSKAIA and E. I. TROFIMOVA

After our investigations ([1], [2], [3], [4]) had disproved those schemes which assumed that in the biochemical formation of citric acid from sugar, the latter is first split up in a way similar to the fermentation of alcohol, and had shown that the whole carbon chain in the sugar takes part in the formation of the acid, the number of possible propositions in explaining the transformation of sugar into citric acid was limited to schemes satisfying the condition just mentioned. Schemes of this kind, which assume that the whole sugar particle participates in the formation of citric acid, include such ones as those of Raistrick and Virtanen ([5],[6]), Franzen and Schmidt ([7]) and that of Butkewitsch ([8]).

The Raistrick-Virtanen scheme, which assume that hexose splits up into oxaloacetic and acetic acids which then condense into the citric acid molecule, was confirmed to some extent by Knoop and Martius ([9]) who worked out a chemical synthesis based on this scheme. Lately, however, in spite of the data given by Krebs ([10]) as to the existence of an analogous process in animal tissues, Breusch ([11]) showed that although this synthesis can be accomplished under certain conditions as a chemical process, it does not occur under physiological conditions.

The Franzen-Schmidt scheme, according to which the transformation of sugar into citric acid goes through phases of sucric and ketipic acids, was not confirmed in the investigations made by Bernhauer ([12]). Walker ([13], [12]), who had accepted the scheme at one time, also failed to find any experimental basis for it.

Butkewitsch's scheme assumes that an aldol condensation takes place in the hexose carbon chain through the aldehyde or ketone group, which either was already present in it or was formed as a result of oxidation. Then the five-atom ring thus formed splits up, giving a branched chain peculiar to citric acid.

While discussing this scheme the authors of it pointed out glucuronic acid as being one of the possible intermediate phases of the transformation according to the scheme. On the basis of this supposition the experiments described below were made, concerning the action of a fungus film upon a solution of glucuronic acid, which has been placed under it.

There is a paper by Hofman ([14]) reporting experiments with *Asperg. niger* culture on glucuronic acid. Only oxalic acid was discovered in the culture, and no citric acid was found. In this case, however, the latter negative result cannot be accepted as final, since the experiment was too prolonged (35 days

at 25°). If citric acid were formed under such conditions, it might have been oxidized into oxalic acid. Gluconic acid was tried in our experiments along with glucuronic acid. The latter was obtained after the method described in Quick's work ([15]) from a dog's urine, after borneol had been added to its food; the former was obtained from *Asperg. niger* ([16]) by placing it under favourable conditions. Both acids were introduced into the experimental solution as salts of sodium. Sodium acetate (in a concentration corresponding to 2.5 per cent of acetic acid) was also introduced along with the salts of these acids, in order to protect the citric acid produced against consumption [see our former works ([1])].

The experiments were conducted in the ellipsoidal flasks generally used by us, which had a tube underneath in order that the solutions may be changed. First of all *Asperg. niger* (strain IV) films were cultivated 3 days in the first experiment and 2 days in the second, using the usual nutritive solution, which contains 5% sugar and 0.3% NH_4NO_3. After the nutritive solution had been removed from under the cultivated films, and the films had been washed, it was replaced with an experimental solution (100 cm³), the composition of which is given in the tables below. The films were raised and kept in the experimental solutions at about 30° in the first experiment and at about 33° in the second. In both cases the films were kept in the experimental solutions for 24 hours, then the solutions were poured out and analysed. The average results of the two parallel experiments are given in Tables 1 and 2.

Table 1

Experiment with Gluconic Acid

Initial experimental solution 100 cm³		Experimental solution after 24 hours (30°)					
		Acetic acid, %	Glucose, %	Citric acid, %	Oxalic acid, %	Reaction of the solution	Weight of the film, g
Acetate Na (acetic acid 2.5%)	—	1.73	—	0	0.20	Alkaline	0.90
	Glucose 2.5%	1.96	1.45	0.08	0.06	Acid	0.92
	Gluconic acid 2.5% (as a Na salt)	1.50	—	0.03	0.30	Alkaline	1.02
Glucose 5%		—	3.22	0.14	0	Acid	1.36

The results quoted show that some citric acid accumulated both in experimental solutions containing gluconic acid and in those containing glucuronic acid, but this accumulation was much less pronounced than in glucose solutions of the same concentration.

Thus, the results of these experiments cannot affirm the hypothesis as to whether glucuronic acid participates in the formation of citric acid from glucose, nor are they grounds enough to disprove it. Under the conditions of this experiment the accumulation of citric acid in the solution was determined not only from the tranformation of the test-substance into acid in the cells, but also by the diffusion of this substance from the solution in the cells. The reason why citric acid accumulated less on the glucuronic acid solution than on the glucose solution lies probably in the fact that the former penetrates into the mycelium cells more slowly. This is affirmed to some extent by the fact that the fungus film on the whole consumes very little glucuronic acid in comparison with glucose. In the second experiment their consumption from solutions of the same concentration was respectively: 0.17 g and 0.85 g.

Table 2

Experiment with Gluconic and Glucuronic Acids

Initial experimental solution 100 cm³		Experimental solution after 24 hours (33°)						
		Acetic acid, %	Glucose, %	Glucuronic acid, %	Citric acid, %	Oxalic acid, %	Reaction of the solution	Weight of the film, g
Acetate Na (acetic acid 2.5%)	—	1.15	—	—	0	0.48	Alkaline	0.84
	Glucose 1%	1.38	0.15	—	0.12	0.34	»	1.02
	Gluconic acid 1% (as a Na salt) . .	1.47	—	—	0.02	0.37	»	0.81
	Glucuronic acid 1% (as a Na salt) . . .	1.27	—	0.83	0.02	0.31	»	0.90

The dry weight of initial (control) films 0.96 g.

In control solution kept under films and containing 2% of glucose and 2% of free gluconic and glucuronic acid without acetate no citric acid was detected.

The amount of glucuronic acid was determined after the method of Bertrand according Kertesz' s table ([17]).

Hamburger's ([18]) data on isomeric forms of glucose and the work of Sobotka, Holzman and Reiner ([19]), published recently, show how great the difference in the velocity of penetration of various substances into living cells can be, even if they are very similar in character and differ only in insignificant peculiarities of structure. The experiments of Sobotka, Holzman and Reiner on yeast cells and various sugars showed that for glucose and xylose the velocity of diffusion into cells is several times greater than for ramnose and arabinose.

Along with the deliberations mentioned above it is necessary to take into account that besides *d*-glucuronic acid which was tested by us, other compounds may have participated in the transformations assumed by the scheme in question. This has already been pointed out by the author before ([8]) and his recent investigations give new indications as to the possible character of these compounds. Data on this subject will be examined by one of us in a special paper.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

BIOCHEMISTRY

ON THE QUESTION OF INTERMEDIATE PHASES OF BIOCHEMICAL TRANSFORMATION OF SUGAR INTO CITRIC ACID

By V. S. BUTKEWITSCH, Corresponding Member of the Academy

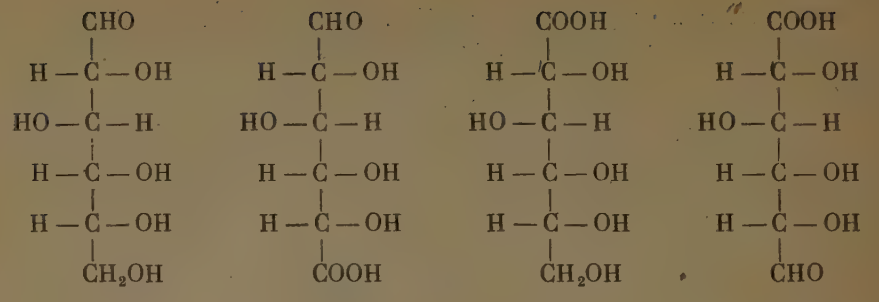
The field of distribution, known up to this time, of citric acid as a product of metabolism in living organisms has lately been greatly expanded. It is no longer limited to organisms of the vegetable kingdom. The latest investigations ([1], [2], [3]) have established that citric acid is constantly present in the tissues and excrements of various animal organisms, in which it is evidently a usual product of normal metabolism.

As to the biochemical tranformations which lead to the formation of this widespread product of metabolism in vegetable and animal organisms, there is a series of data which prove their connection with carbohydrate interchange ([4],[3]).

As early as in 1924 the author of this paper tried to connect the origin of citric acid with the transformation of carbohydrates and also to show some possible ways of changing the latter into former ([5],[6]). The facts which served as basis for the ideas which we developed, have been supplemented lately with some new data. In connection with the scheme of the biochemical formation of citric acid, set forth by us, these data are the topic to be examined in this paper.

In order that the process may be accomplished according to our scheme the six-atom carbon chain which participates in the formation of citric acid should contain an aldehyde or ketone group, where it could shut to form a five-member ring. We have expressed the supposition that in the transformation of glucose into citric acid, glucuronic or diketogluconic acid may be an intermediate phase ([6]).

As to uronic acids, we must bear in mind that when glucose is oxidized, two acids, entirely different in structure, may be formed, viz.: glucuronic which retains the aldehyde group from the glucose, and aldehydgluconic, in which a new aldehyde group is formed as a result of the oxidation of the alcohol group in glucose, while the old aldehyde group turns into a carboxyl group. Gluconic acid is an intermediate phase in the transformation of glucose into aldehydgluconic acid. The relation between glucose and the acids mentioned is made obvious in the following comparison:



d-glucose *d*-glucuronic acid *d*-gluconic acid *d*-aldehydgluconic acid

According to the data at hand the formation of both uronic acids mentioned is possible during the biochemical transformation of glucose.

It has been known a long time already that *d*-glucuronic acid is formed in animal organisms and is always present in small quantities in urine combined into a pair with some aromatic product of the decay of the protein molecule. The quantity which the organism excretes can be greatly increased by introducing compounds into the organism, capable of forming pair combinations with it (7).

There is some evidence which shows that uronic acids are formed also in vegetable organisms. Erlich and other investigators have established that acids of this category are constant components of pectin substances (8), which are widely distributed in plants.

Glucuronic acid was detected by Wünschendorf and Killian (9) in cultures of the fungus *Ustulina vulgaris* on glucose with peptone, along with malic, succinic, lactic, oxalic and citric acids.

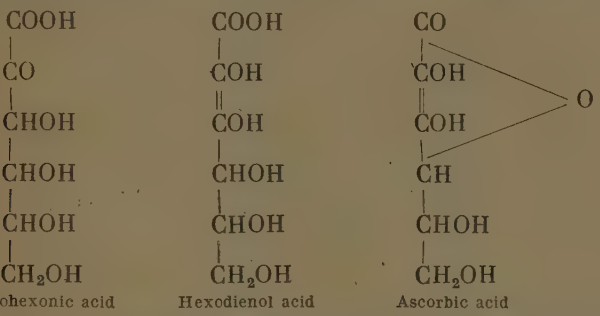
Chouchak's observations (10) also show that some fungi form glucuronic acid. In studying the juice of grapes infected with mouldy fungi he found great quantities of glucuronic acid in it, which increased with the degree of infection, while the juice of healthy grapes was found to contain only traces of it, or none at all.

Palladine and Levtchenko (11) discovered uronic acids among substances formed in *Asperg. niger*. Heidelberger and Gabel (12) found them in patogenic bacteria, and Hopkins, Peterson and Fred (13) in nodule bacteria.

A recent work of Takahashi and Asai (14) contains data on aldehydgluconic acid. They observed its formation from glucose and also from gluconic acid in cultures of *Bact. industrium* var. Hoshigaki. Later Bernhauer and his collaborators (15) showed that other acetate bacteria also produce this acid.

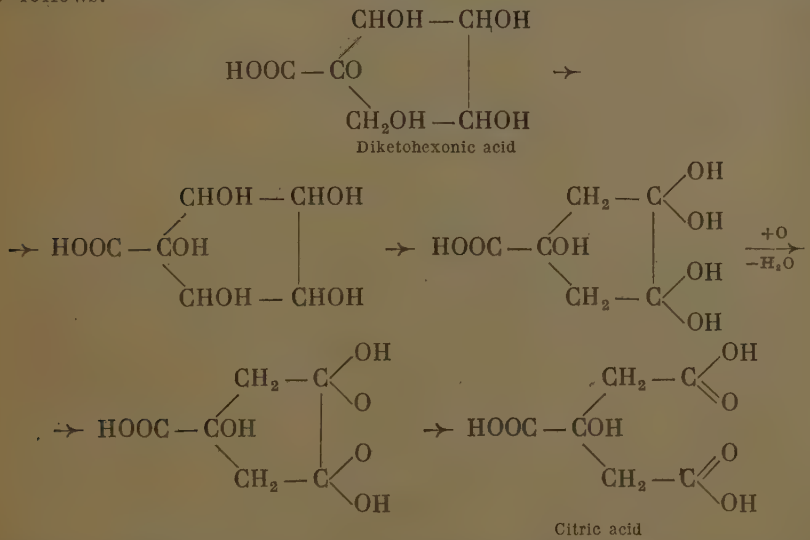
In the experiments conducted by us (16) in producing citric acid with films of *Asperg. niger*, only *d*-glucuronic acid was tried. Some citric acid was formed in the experiments with it, but much less than in similar experiments conducted with glucose. Thus, the results of these experiments cannot be accepted as final in solving the problem as to whether glucuronic acid participates in the formation of citric acid from glucose, or not. It is possible that when glucose is transformed into citric acid, the intermediate phase is not *d*-glucuronic acid, which was tested by us, but aldehydgluconic or, even more probably, diketogluconic acid. The latter was discovered recently by Bernhauer and Görlich (17) along with aldehydgluconic and pentaketogluconic acids, among the products of the transformation of glucose and gluconic acid by certain acetate bacteria.

Besides that, recent works ([15], [19], [20]) dealing with the structure of ascorbic acid (vitamin C) lead to the conclusion that diketohexonic acids are transformation products of hexose, which is widely distributed in the vegetable kingdom. As has definitely been proved by its synthesis, ascorbic acid is itself a lactone of a diketohexonic acid in dienol form, and this acid is apparently an antecedent of ascorbic acid in its formation from hexose. The following comparison gives an idea of the relation between ascorbic acid and diketohexonic acid.



Diketohexonic acid — Hexodienol acid — Ascorbic acid

According to our scheme of the biochemical formation out of hexocitric acid, the diketohexonic acids may be antecedents of the hexocitric acid as well. The transformation of ketohexonic acid into citric may be represented as follows.



Citric acid

This transformation of hydroxyl groups, which we see in this scheme, takes place in many biochemical sugar transformations. Such a transposition takes place also in the saccharine regrouping described by Kiliani ([21]) and later also by other investigators ([22], [23]). There is enough evidence from well-established chemical transformations ([24], [25]) to give grounds to the formation of a ring compound as assumed in the scheme, and to the subsequent rupture of the ring due to oxidation.

The weakness of the scheme given above when we were figuring it, was the absence of any more or less definite data on the formation of aldo- or keto-

hexonic acid during biochemical transformations, as an intermediate phase in it. At present this weakness in the scheme is being removed, since data obtained lately show that the acids assumed in the scheme to be intermediate phases are a widely distributed product of the biochemical transformation of hexose. These data give our scheme a certain biochemical basis which it did not have befor.

New data recently published by Bond, Knight and Walker ([26]) on the capability of some fungi to oxidize glucose into glucozone may be added to those given above. The ketone group in the latter occupies the same position as in diketohexonic acids, i. e. a position favouring those transformations which take place according to the scheme given above.

In connection with the possibility of the existence of a common antecedent for ascorbic and citric acids, attention should be called to the fact that one of the two acids is just as widespread in the vegetable kingdom, as the other, and a number of cases can be named, where it has been firmly established, that they occur together in well-known vegetable objects. Such objects include, for instance, the citrous fruits, cabbage leaves ([27]) and tomatoes ([28], [29]) which are rich in vitamin C. Lemons and oranges, being richest among the fruits in vitamine C ([30]), have at the same time an ample quantity of citric acid. This gave rise to the popular prejudice about the antiscorbutic properties of citric acid ([31]).

Actually, as has been definitely determined, it is not the citric acid that possesses these properties, but the ascorbic acid which occurs together with it.

On the basis of the facts and deliberations given above, we believe that the investigations conducted by us on the formation of citric acid from glucuronic should be extended to other acids, similar to it in structure, viz.: to aldehydgluconic and particularly to diketohexonic acids. The participation of the latter in the formation of citric acid according to our scheme becomes quite probable as a result of the data which we now have at hand.

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Received
9. II. 1938.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

GEOLOGY

ON THE SALAÏR FOLDING

By K. V. RADUGIN

(Communicated by V. A. Obruchev, Member of the Academy, 12. II. 1938)

In the summer 1937 the present author had to guide a student's geological practice in the region of the Mount Orlinaya near the Guryev works. This picturesque spot of West Siberia lying along the north-eastern border of the Salaïr range is very interesting for a study of the stratigraphy and tectonics of the Paleozoic. Though it had been already studied by a number of geologists, e. g. B. F. Speransky, I. S. Zeiklin, V. I. Yavorsky and others ([1], [2], [5], [6], [7], [8], etc.), and a map of the region, on a 1:25000 scale, had been drown, still it proved possible to make there new and significant observations and to come from these to important conclusions. The aim of the present paper is to acquaint persons interested in the geology of Siberia with some of these conclusions referring to the Cambrian folding.

The Cambrian folding movements, the establishment of which is a great achievement of the Soviet geology, have been at present accepted by a number of geologists. Owing to numerous tectonic movements of the Cambrian age, the geosynclinal character of the Cambrian of South Siberia and the tectogene type of its development have recently been established ([4]).

Apart from Gornaia Shoria the area of Mount Orlinaya near the Guryev works is so far the only place in West Siberia where the presence of the Upper Cambrian has been proved palaeontologically, and where, in consequence, the age of the tectonic movements of the Upper Cambrian may be exactly established.

The facts which may be observed here are as follows: in the area of the ridge of the anticline of Mount Orlinaya (Fig. 1), $1^1/_2$—$1^3/_4$ km south-east of the former Krekov mill, the Cambrian limestones of the eastern side of the anticline are outcropping from under the turf on the top of a steep slope and are terminating there. Somewhat below in a soil outcrop the same limestones are seen, a conglomerate being present too. The limestones are of a greyish-white colour; they are intersected by rather closely-spaced vertical schistous fractures in the NNW direction. Separate fractures of the same direction are occasionally observed in the conglomerate, but these are rare, since the schistosity of the limestones does usually not penetrate into the conglomerate, the latter being thus almost unaffected by schistosity. The surface of the contact of the conglomerate and the limestone is sharply unconformable both with the schistosity and the general almost meridional strike of the Cambrian limestone. This surface dips about 330° NW at an angle of 30°.

Thus a sharp angular (almost rectangular along the strike) unconformity between the *Cm* limestone and the comglomerate is observed here. In connection with this the behaviour of the above mentioned schistosity can easily be explained, evidently it has chiefly originated previous to the conglomerate and only part of the fractures have enjoyed a subsequent development and have penetrated into the higher lying comglomerate. The latter is composed of small smooth pebbles, among which a sealing-wax jasper should be noted forming metasomatic vein-like inclusions in the underlying limestone. The surface of the unconformity has been affected by subsequent emanations accompanied by a formation of hematite and barite. Finally, it is of interest to note that the *Cm* limestones show traces and remains of an

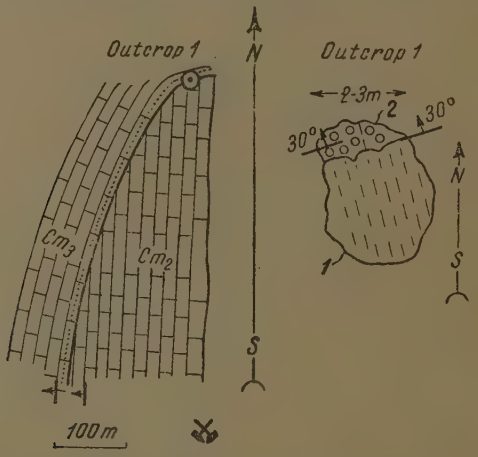

Fig. 1. Relation between limestones Cm_3 and Cm_2, Mount Orlinaya. *1*—Schistosity of limestones Cm_2. *2*—Basal conglomerate.

ancient (Cambrian) weathering crust under the conglomerate and alongside of it, which are particularly distinct southward, on the slope of Mount Orlinaya composed of the same limestones. Up to that place we can follow the above mentioned contact of limestones with comglomerates and sandstones, the latter being essentially calcoarenites. There these horizons are overlain with a layer, composed of schists, sandstones and limestones. It is from the latter that originates the author's first collection of the Upper Cambrian trilobite fauna (²) (Fig. 1, exp. 21—a—b; 22); in 1937 the author found there also algae of the *Solenopora* or *Cryptozoon* type. On the other hand, points with Middle Cambrian trilobites (²) (Fig. 1, exp. 12 and 12bis) are located, stratigraphically, below the unconformable contact established in the described basset. In this way the age of one of the Cambrian foldings (at the boundary between Cm_2 and Cm_3) is well determined, the more so that the authors determinations of age have been recently supported by E. V. Lermontova (¹). We assume, that this folding is younger than the Guryev folding and older than that of Berikul, established by M. A. Ussov (⁶) (202, plate II). For this folding the name of Salaïr is retained following the suggestion of A. M. Kuzmin [(³), 53].

Southward from the outcrop described the angular unconformity of Cm_3 bedding over Cm_2 evidently disappears since the Cm_3 beds acquire practically the same strike (and probably also the dip) as that observed in the beds of the Cm_2 limestones. Consequently we have here to do with a rather fre-

quent case of inherited (according to Stille) folding, where previously bedded folded structures develop with preservation of their strike. This case is very instructive for those who only from one or several intersections of the foldings conclude, as it may be frequently seen in our literature, in favour of a perfect conformity of two beds, which is essentially wrong.

Thus, the following course of events seems to have proceeded at Mount Orlinaya at the close of the Middle Cambrian. After the marine conditions, under which the pure trilobite limestones of the upper portion (1) of the Middle Cambrian had deposited [evidently the Berezov formation (3) of the Middle Cambrian], these limestones underwent dislocations which produced foldings and schistous fractures appeared in the NNW strike. They were also subject to metasomatosis with a formation of red sealing-wax jasper. The latter phenomenon should be connected with the magmatic processes of the close of the Middle Cambrian. Further in the area of the saddle of the Mount Orlinaya anticline, denudation processes took place with an erosion of limestones (Berezov formation) and effusives of the Middle Cambrian cropped out. Near by on the same limestones a red-coloured weathering crust developed under conditions of sinkhole formation. Then the Upper Cambrian sea advanced, and basal sandstones and conglomerates of the Upper Cambrian were formed.

The area of Mount Orlinaya presents interest for inquiring into the Silurian and Devonian tectonic movements. Without discussing this question, I conclude this paper with inferences regarding the Ostracoda limestones and the overlying deposits.

An exact mapping of their boundaries shows that a number of unconformities exists in these apparently continuous beds, particularly in the footwall and hanging wall of the Ostracoda limestones. Unconformities are also observed in the Middle Devonian. The type of these unconformities is an evidence for more or less strong folding movements.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

GEOLOGY

THE EOCENE SEDIMENTS OF THE TUAPSE REGION

By B. M. KELLER

(Communicated by A. D. Arkhangelsky, Member of the Academy, 19. II. 1938)

A conspicuous peculiarity of the flysch beds, developed along the southern slope of the Great Caucasus, consists in the uniformity and persistency of their petrographic composition along the strike. At first sight the beds of different age composing the flysch also seem to be uniform and similar to each other. They have, however, only one feature in common, viz., the alternation of rocks of a different lithological composition. After a careful examination specific peculiarities may be established for each series, which distinguish the rocks of the same age. If we had drawn an available stratigraphic scheme for the region of the development of the flysch, we could after the lithological characters positively discriminate the principal ages within a large area, quite so as it is done in any other region. This scheme, however, is difficult to be drawn. The tectonic structure of the flysch being complicated, it is not always possible to make out the normal sequence of the series, while the palaeontological method fails on account of the rare occurrence of organic remnants. New palaeontological findings often require a reconstruction of the scheme already admitted. One of those findings, discovered in the Tuapse region, is the subject of the present note.

In the summer of 1937 a study was made of the Upper-Cretaceous section in the vicinity of Tuapse, and the author came across a singular series of flysch sediments, developed along the sea coast in the area of the town of Tuapse and at the issue of the Pauk-river.

These beds consist of an alternation of soft light-green and almost black argillaceous marls, siliceous rocks, quartz-glauconite fine-grained sandstones with siliceous or calcareous cement and limestones. The limestones, sometimes entirely organogene, consisting of foraminifers spicules of sponges and fragments of other organisms, contain aggregates of half-smoothed quartz grains. Light-grey, almost white limestones, consisting entirely of micrograined calcite are occasionally encountered. Siliceous seams (silicites) of a grey or dark-grey colour, very characteristical of the beds under description, contain small quantities of spicules of sponges. In order to give a clear idea of the stratification of rocks, the author gives a description of the successive layers in a small portion of the section, made at the sea coast, west of the issue of the Pauk-river.

1. Light-coloured, bluish argillaceous marl with two compact bands
2. Dark-grey compact marls
3. Light-grey, almost white compact limestones
4. Dark-coloured calcareous marl
5. Light-grey silicite
6. Light-coloured calcareous clay
7. Grey-coloured compact sandstone
8. Dark-coloured, argillaceous finely laminated marl
9. Dark-coloured silicite

From their lithological peculiarities the beds described are very like the Eocene sediments of the Sochi region, and as the presence of the Eocene in the Tuapse region has not been previously known*, particular attention was given to the search for seams which are likely to contain foraminifers. The latter were found in the soft, green, argillaceous, slightly arenaceous marls, containing a fauna of a peculiar composition. V. G. Morozova, who undertook the identification of the fauna, reports the following species: *Trochamminoides irregularis* white, *Bolivinoides aragonensis* Nuttab, *Gumbelina* sp., *Globorotalia aragonensis* Nuttab, *G. aragonensis* var. *caucasica* Glaesner, *G. crassata* var. *olensa* Cushman, *Globigerina bulloides* d'Orbigny, *G. triloba* Reuss, *G. compressa* Plummer, *Eponides Frumpeii* Nuttab, *E. umbonata* Reuss, *Anomalina grosserugosa* Gumbel.

The above fauna undoubtedly pertains to the Eocene age. It is characteristical of the horizon F, the so-called foraminiferal layers of the Northern Caucasus, the age of which has been determined recently as the Lower Eocene.

The finding of Eocene fauna within the horizon of siliceous rocks necessitates a revision of the stratigraphy and tectonics of the littoral part of the Tuapse region, the geological structure of which was studied in detail by O. S. Vyalov in 1930 and 1931.

The Eocene bed with siliceous seams has been isolated by O. S. Vyalov under the designation of the spongolite horizon, composed of «light-coloured silicified strata, projecting as thin cornices among darker clays and marls». According to O. S. Vyalov's data the spongolite horizon was located stratigraphically between the rocks of the Dederkay series and the overlying dark marls of the Agoy** series. At present it has been found that this horizon belongs to considerably younger deposits, and it may be supposed that both in the Tuapse region and in other regions of the Western Caucasus, the light-coloured flysch is gradually replaced by the rocks of the Agoy series. At the same time, the line of break, which was drawn by S. O. Vyalov between the light and dark-coloured flysch south-west of Tuapse, becomes useless. Vyalov had no other grounds to trace this line but the absence of the spongolite horizon between these two series. We should modify our conception of the tectonic structure, which has been determined by the appearance of a silicified pack between two bands of dark flysch*** and considered by O. S. Vyalov as an anticlinical fold. As a matter of fact, this essentially synclinal structure is, evidently, clipped along its south-western edge by a considerable overthrust with a plane of disruption, dipping in the direction of the sea. Thus, the problem of the presence of complex tectonic disturbances, bringing into contact the spongolite horizon and the rocks of the Upper Cretaceous, should be solved for the Tuapse region.

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* V. E. Pchelinzev, who in 1927 drew a geological map of the Tuapse region according to the views of the geologists of Kuban, referred the series of dark-coloured marls and the overlying sandstones of the Goryachy Klyutch series to the Eocene. It turned out later that these rocks belong to the Paleocene and older beds.

** The Dederkay series (light-coloured flysch) may evidently be referred to the Campanian; the Agoy series (dark-coloured flysch), to the Maestrichtian.

*** See the geological map of the Tuapse region, drawn by O. S. Vyalov ([1],[2]).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

MINERALOGY

ON THE CHARACTERISTIC OF THE MINERAL «MONOTHERMITE»

By D. S. BELIANKIN, Corresponding Member of the Academy

We met first this mineral about 6—7 years ago under the following circumstances. In the summer of 1931 the scientific collaborator of Ceramic Institute J. B. Kaler asked for our consultation on the occasion of a somewhat vague microscopy of a preparation of Chassov-Jar clay, which she had investigated. According to V. I. Iskule's and T. E. Krasenskaia's data (1929) the mineral composition of this clay should essentially consist of three minerals: kaolin, quartz and muscovite, but in Kaler's preparation the finely lamellar muscovite could only be distinguished. We were extremely interested in this phenomenon and in order to understand it better we investigated Kaler's preparation more thoroughly, as well as several other preparations of the Chassov-Jar clay and of clays similar to the latter, as the Popasniansk, Gubino and other clays.

We found that the phenomenon was repeated, but the substance which first seemed to be muscovite or sericite, should be rather considered, due to its refraction ($N=1.55—1.57$), as a mineral of kaolin group. Crystallo-optically it differs from the typical kaolin only by the increased birefringence: $Ng—Np=0.02—0.03$ (for kaolin it is 0.006; for muscovite, 0.04).

In the autumn of the same year the Chassov-Jar clay was independently of us studied by K. G. Kumanin, who defined its another extremely curious property: the only one endothermal effect at 550° on its heating curve instead of two effects proper to real kaolin: 1) the same endothermal one and 2) the exothermal one at 900—950°. After K. G. Kumanin had privately informed us about this fact the same thermal analysis was repeated by H. S. Nikogosian with our materials. The results coincided exactly with those obtained by K. G. Kumanin. The materials of this latter investigator kindly placed by him at our disposal proved to be microscopically identical to ours.

In order to attract the attention of specialists to the newly stated by Kumanin and us original mineral we called it X-mineral and published about it a note in the Bulletin of Ceramic Institute, 1932, № 1, p. 10—15. In this note we tried, by the way, to approach at least approximately to the chemical composition of X-mineral and for this purpose used: 1) chemical analysis of the material studied by K. G. Kumanin made by the Leningrad Works of Optical Glass and 2) comprehensive analytical material from V. I. Iskule's work (1929). The table represents somewhat shortened data reported in the mentioned above Bulletin with addition of a new chemical analysis made later on our material by G. B. Prigozhina.

	1	2	3	Average from 2 and 3	Molecular quantities	
SiO_2 . . .	52.56	53.98	54.31	54.15	0.9016	
TiO_2 . . .	0.60	1.29	1.03	1.16	0.0145	
Al_2O_3 . . .	33.11	31.12	30.42	30.72	0.3014	
Fe_2O_3 . . .	1.06	0.97	1.18	1.07	0.0067	
MgO . . .	0.03	0.49	0.48	0.48	0.0119	0.072
CaO	0.56	0.78	0.57	0.67	0.0120	
Na_2O . . .	3.56	0.65	0.44	0.54	0.0087	
K_2O		2.60	2.98	2.74	0.0397	
SO_3	not defined	0.07	0.20	0.13	—	
Humus . .	not defined	0.23	not defined	—	—	
Loss at heat	8.32	8.47	8.39	8.43	0.4679	

Remarks. 1. Analysis by the Leningrad Works of Optical Glass. 2. The average from 4 analyses of the Chassov-Jar clays especially investigated at the Ceramic Institute (from V. I. Iskule's work). 3. G. B. Prigozhina's analysis.

From the molecular quantities of the table we may, reducing them to Al_2O_3 as a unit, derive the following approximate chemical formula of X-mineral:

$$0.2\bar{R}\bar{O}\cdot Al_2O_3\cdot 3SiO_2\cdot 1.5H_2O.$$

In 1933 K. G. Kumanin published in Transactions of Petrographical Institute of Academy of Sciences of the USSR a similar article (but without optics and chemical calculations), p. 101—109.

After these publications we continued to take interest in X-mineral and found out that it was more or less essential component of the most part of the Soviet clays. It is quite probable that the same X-mineral is present also in many foreign clays, to which possibillity we should like to attract the attention of our foreign colleagues. Compare, e. g. Ross' and Kerr's data (1930) concerning the muscovite-like mineral from North Carolina. In our further publications we began for a greater certainty to call our X-mineral «monothermite» or endothermite (due to its single and endothermal effect on the heating curve).

As it has been mentioned above, G. B. Prigozhina made a special chemical analysis of monothermite at the Ceramic Institute. Studying this analysis we noticed that it implied not the air dry substance, but the substance dried at 105°, similarly to all other analyses of this Institute. Therefore, by our ask, G. B. Prigozhina has also kindly defined the loss in weight at 105° of her air dry preparation which has bean found to reach 3.12% (mol. quant. 0.1732). Accounting for this so-called «humidity» we obtained for the finite chemical formula of monothermite the following expression:

$$0.2\bar{R}\bar{O}\cdot Al_2O_3\cdot 3SiO_2\cdot 1.5H_2O\cdot 0.5\ aq.$$

At the same Ceramic Institute L. M. Kuprianova studied the limits of dehydration of monothermite at different temperatures. The dehydration curve plotted according to her data is represented in Fig. 1.

According to Prigozhina's data and Kuprianova's diagram we see that the water content in monothermite is almost the same as in normal kaolin. Its somewhat smaller value may be explained, on one part, by insufficient purity of our preparations (admixture of quartz and, perhaps, partly of mica), and on the other, by partial replacement of water in monothermite by the metallic bases and especially by K_2O.

The strength of association of water in both minerals is, however, quite different. While monothermite yields 0.5 H_2O separately from the rest 1.5 H_2O already at 100°, kaolin preserves $2H_2O$ almost entirely up to 300—400° when its energetic separation begins.

However, the more attentive study of this problem shows that this difference is not so sharp.

Let us first of all recollect Kerner and Sahlmang who showed that typical Zettlitz kaolin, when subjected to the isothermal decomposition, i. e. to the dehydration in vacuo at constant temperature, always yielded 0.5 H_2O together with the ordinary moisture. Therefore only 1.5 H_2O may be considered here as chemically bound hydrate water (Sahlmang, 1935, p. 66). Let us further remind Hirsch's and Dawill's experiments concerning the double exchange between the Zettlitz kaolin and molten nitrous potassium at 500°.

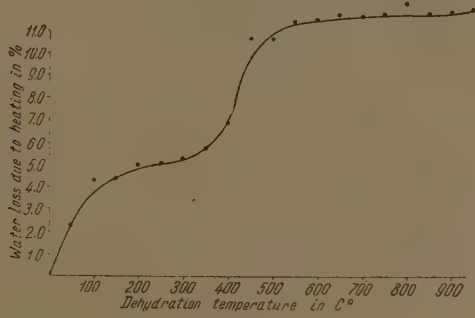

Fig. 1.

Only 0.5 H_2O of kaolin were exchanged with K_2O of saltpetre, consequently just that its quantity which is comparatively not so strongly bound with kaolin composition, i. e. similarly to the case of monothermite. By the way, it is characteristic that the experiments of double exchange with saltpetre repeated by L. M. Kuprianova, using Preobrazhensky kaolin and Chassov-Jar monothermite, gave quite similar results with those obtained by Hirsh and Dawill.

As we have seen above, monothermite compared to normal kaolins is richer in SiO_2 and contains a considerable quantity of bases (K_2O).

As to the first instance, it may be explained, on one part, by small admixture of quartz in our preparations and, on the other part, some excess of SiO_2 may be included in the very constitution of monothermite, similarly to some kaolins enriched in excess with SiO_2 (almost up to the same ratio 1 : 3 between Al_2O_3 and SiO_2, after Ross and Kerr, 1930).

Concerning K_2O we may repeat the hypothesis mentioned above, that it is included at least partially into the very molecule of monothermite. Just this instance explains also, in our opinion, the special peculiarities of monothermite: 1) its increased birefringence and 2) absence of the exothermal effect on its heating curve.

The essence of the exothermal reaction of kaolin, as we stated before, consists either in association into a molecule of mullite of finely dispersed Al_2O_3 and SiO_2, formed at kaolin dehydration (our explanation), or in the crystallization of amorphous alumina into γ-Al_2O_3 (Insley's explanation, 1935).

It is of a small importance which of these two explanations is accepted, but the mineralizing effect of K_2O must in any case help to the premature

(at lower temperatures) crystallization of γ-Al_2O_3, which prevents the exothermal development of reaction at higher temperatures (compare D. S. Beliankin and V. P. Ivanova, 1936; D. S. Beliankin, 1937).

Received
15.II. 1938.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

GENETICS

ON POLYMORPHIC TYPE OF SPECIES' ORIGIN

By M. A. ROZANOVA

(Communicated by N. I. Vavilov, Member of the Academy, 9. II. 1938)

In recent years much attention has been given in literature to the problem of amphidiploidy. The creation, as a result of hybridization, of new, constant, or relatively constant, forms (amphidiploids), having a chromosome number equal to the combined chromosome numbers of the two parents, has been reported in very different families, genera, and species. These so-called species novae—although not species in the evolutionary sense, since their viability has not yet been put to the test—serve as proof that new species may arise as a result of amphidiploidy.

Other experiments have shown that species verae, i. e., species occurring in nature, may, in a similar way, be obtained synthetically. Although instances of such synthetic creation of species are not numerous as yet, they indicate clearly the significance of amphidiploidy in species-formation. Among species verae obtained experimentally are the following: *Galeopsis Tetrahit* ($n=16$), obtained by Müntzing (1930, 1932) by crossing *G. pubescens* ($n=8$) and *G. speciosa* ($n=8$); *Phleum pratense hexaploidium* ($n=21$), a form occurring in nature, by Gregor and Sansome (1930) and Gregor (1931) by crossing *P. pratense* ($n=7$) and *P. alpinum* ($n=14$); *Rubus maximus* ($n=21$) by Rozanova (1934) by crossing *R. idaeus* ($n=7$) and *R. caesius* ($n=14$); *Prunus domestica* ($n=24$) by Rybin (1935, 1936) by crossing *P. spinosa* ($n=8$) and *P. divaricata* ($n=16$).

The synthetically obtained species are not necessarily absolutely identical to species existing in nature, since the latter have already passed through a definite stage in their evolutionary development. But, in view of the fact that the differences are not marked and in view of the polymorphism of the species in nature, it is difficult to define precisely these differences at the present time. This requires further study and comparison of the natural and synthetic species.

The fact that it is possible to create species by means of amphidiploidy having been established, it must be granted that it is also possible that species may originate in a polymorphic state.

Polymorphism in the progeny of amphidiploids has been ascribed to the following causes. First, the homology of some of the chromosomes of the species which gave rise to the amphidiploid. In such a case there may be formed at meiosis multivalents and, consequently, gametes with aberrant chromosome numbers, which leads to the formation in the progeny of chro-

mosomal aberrants (Buxton and Newton, 1928; Lammerts, 1931, 1932; Poole, 1932; Skalinska, 1932). Second, the non-conjunction of some of the homologous chromosomes, which also leads to the formation of gametes with aberrant chromosome numbers. Müntzing (1935) ascribes this phenomenon to incompatibility between the maternal plasma and the chromosome set of the other parent. Third, the heterozygosity of one or both parents, leading to segregation with respect to those characters for which the parents are heterozygous (Karpechenko, 1935).

In addition to these causes for the origin of polymorphic species, we have ascertained, in the course of obtaining the synthetic species *Rubus maximus*, two other causes:

1. A polymorphic species may at once result, if the species giving rise to amphidiploidy belong to different races. When the areas of the parental species overlap, the different races may interbreed and, consequently, there may arise throughout the entire area amphidiploids of different types. Hence, the new species will at once constitute a complex «conspecies».

2. A new polymorphic species may at once arise, if from the hybridization of two species there result not only amphidiploids, but also forms with other genomic combinations that may prove viable.

Without giving in detail the data already presented by us in our earlier paper on the production of the synthetic species *Rubus maximus* (Rozanova, 1934), we shall cite here only those facts which may throw light on our suppositions regarding the polymorphic type of origin species.

In crossing *Rubus idaeus* L. with *R. caesius* L. different races gave different results, fertile progeny being obtained only in two cases, viz., when *R. idaeus* was crossed with the Perm or with the Turkestan race of *R. caesius*. The results in these cases were as follows: The F_1 from the cross between *R. idaeus* ($n=7$) and the Turkestan race of *R. caesius* ($n=14$) was almost sterile, having, as was to be expected, 21 chromosomes. Analysis of meiosis in this hybrid showed that at the first division there is observed that type of restitution nucleus which leads to the formation of gametes with the somatic chromosome number. Such gametes are, apparently, formed very rarely, and the percentage of normal pollen ranges from 2 to 6. The setting of fruit, which occurs rarely (in the form of single drupelets) under conditions of open pollination, may be the result of the fusion of two unreduced gametes of the given hybrid or of an unreduced female gamete of the hybrid with a normal gamete of one of the parents (since in the nursery the parental forms were growing near the hybrids). In the former case occasional amphidiploids arise; in the latter 28-chromosome (if pollinated by *R. idaeus*) or 35-chromosome (if pollinated by *R. caesius*) hybrids. The progeny of amphidiploids proved to be karyologically constant (as regards their morphological constancy, it is difficult to judge due to the small size of the seedlings); progeny from the 28- and 35-chromosome hybrids have not yet been obtained.

The cross between *R. idaeus* and the Perm race of *R. caesius* gave an F_1 either of sterile 21-chromosome individuals or of fertile 28-chromosome ones. The latter, presumably, are the result of the fusion of an unreduced gamete (14 chromosomes) of the mother plant, *R. idaeus*, with a normal gamete (14 chromosomes) of *R. caesius*.

In view of the fact that in the 28-chromosome hybrids the stamens are undeveloped, self-pollination cannot occur. When these hybrids were crossed with *R. idaeus* ($n=7$), there was obtained only 28-chromosome progeny. When crossed with *R. caesius*, the set of seeds was poor, and all five plants obtained were 35-chromosome plants. Since it has not yet been possible to make a cytological investigation of macrosporogenesis, the viability of the

gametes may be gauged only by an analysis of the progeny. Such an analysis shows that in the 28-chromosome hybrid only 21-chromosome gametes prove to be viable.

If we designate the haploid genom of *R. idaeus* ($n=7$) by the letter *I* and that of R. *caesius* ($n=14$) by *CC* (we do not yet have data for the differentiation of these genoms), the hybrids obtained from the two crosses will have the following formulas:

ICC ($2n=21$)—sterile or almost sterile F_1 hybrid.

IICC ($2n=28$)—fertile F_1 hybrid from the cross *R. idaeus*×*R. caesius* (Perm race); fertile F_2 hybrid from the cross *R. idaeus*×*R. caesius* (Turkestan race) ×*R. idaeus*; and fertile F_2 hybrid from the cross between the 28-chromosome hybrid *R. idaeus*×*R. caesius* (Perm race) × *R. idaeus*.

ICCCC ($2n=35$)—comparatively fertile hybrid from the cross between the 28-chromosome hybrid *R. idaeus*×*R. caesius* (Perm race) × *R. caesius*, and from the cross *R. idaeus*×*R. caesius* (Turkestan race)×*R. caesius*.

IICCCC ($2n=42$)—fertile amphidiploid from the F_2 from the cross *R. idaeus*×*R. caesius* (Turkestan race).

Of the above hybrids the amphidiploids and the 28-chromosome hybrids from the cross *R. idaeus*×*R. caesius* (Perm race) are very similar in their characters to *R. maximus* Marsson; the other hybrids also have characters of species of the series *Sub-Idaei* (to which *R. maximus* belongs). In other words, these crosses elucidate the origin of the series *Sub-Idaei* and explain its polymorphism. Focke, in establishing the series *Sub-Idaei*, included in it at first one species with four subspecies (1904), later two species (1914). This indicates that the series *Sub-Idaei* is polymorphic and that the boundaries of the species are not precise.

As a result of our experiments the polymorphism of the series *Sub-Idaei* may be readily understood. Some of its forms or species, being amphidiploids, will be constant or relatively so; others will be variable as regards their genomic constitution, depending on the type of gametes entering into combination. In nature the series *Sub-Idaei* is found in southern Sweden, Denmark, and northern Germany. We found one 35-chromosome plant closely resembling species of this series near Kirov (formerly Viatka). In other words, the series *Sub-Idaei* is distributed in those localities where the areas of the species *Rubus idaeus* and *R. caesius* overlap and where the ecological conditions favour natural hybridization of these species.

Thus, our experiments have disclosed processes taking place in nature, and the observation of species in nature has confirmed our experiments.

In pointing out the possibility that species may originate as polymorphic species, it should be noted that we concede that there may also be a monomorphic type of origin of species, polymorphism arising subsequently. In case a species originates in a polymorphic state, its polymorphism will usually embrace its entire area; in case it originates as a monomorphic species, the polymorphism developing subsequently may either embrace the entire area or be concentrated in localities with definite ecological conditions. In the latter case the type of polymorphism depends upon the ecological conditions in which the species finds itself and upon its differentiation. In case of extreme differentiation of the species, there are more chances that its polymorphism will embrace the entire area of distribution; in case of slight differentiation—that it will be more concentrated. Hence, the type of polymorphism is a function of the mode of origin of the species, its differentiation, and the ecological conditions in which the given species is found.

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Received
9. II. 1937.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

GENETICS

COMPOSITION OF BLOOD IN CAMELS IN RELATION TO THE WORKING ABILITY OF THESE ANIMALS

By H. F. KUSHNER

(Communicated by N. I. Vavilov, Member of the Academy, 5. II. 1938)

Blood performs most vital functions of the body such as carrying food, oxygen, hormones and decay products, protective functions, thermotaxis, and so on, and, naturally, the attention of the investigator, in his search for the agent affecting the productivity of animals utilized in agriculture, is more and more directed to the study of blood components; the more so that recent experiments with blood components established the hereditary nature of many of them. Above all it is necessary to point out here that for certain groups of blood their transmission by inheritance has been established. Thus, in the case of horses, cattle, sheep and fowl distinctive hereditary characteristics relating to the quantity of haemoglobin, number and size of erythrocytes, blood alkalinity, have been found by many research workers. In regard to the size of erythrocytes it has been established that the small size of erythrocytes is dominant over the large one. Finally, quite recently, Rosahn and his collaborators([6]), experimenting on rabbits, proved that most of the components of blood studied by them transmitted their qualities by heredity.

In regard to the composition of the blood of horses it has been established by several Soviet scientists([1-7]) that horses with higher indices of the oxidizing power of blood are distinguished for great working ability and high animal spirits. However, no experiments of this kind have so far been made with camels although these animals are highly important for our south-eastern regions.

In October 1937 we made analysis of the blood of 100 camels taken from the pedigree herd of Camel Farm № 125 (South Kazakhstan). The camels had not been put to work. The analysis of the blood was taken for content of haemoglobin, number and size of erythrocytes and blood alkalinity. In every case the blood was taken from the jugular vein in the morning hours before the animals were taken to water and pasture. The content of haemoglobin was determined by Sahli's haemometer, the number of erythrocytes, by means of a Thomas-Zeiss camera; the length and width of the erythrocytes was ascertained by the dry undyed smears after they had been magnified 2400 times, and the blood alkalinity by Nevodov's method.

It is well known that one of the most remarkable characters contained in crossing the C. dromedarius with the C. bactrianus is the heterosis of their F_1 hybrid (nar) in respect of the working qualities and size. Thus, the female camels examined by us weighed: the dromaderies, 621.5 kg, the bactrians, 666.3 kg, while the nars (F_1 hybrids) weighed 708.3 kg. The nars proved superior not only in regard to weight but also in regard to measurements of body, working ability and rate of development of the young. For this reason we have made analyses not only of the blood of the parents crossed but also of the F_1 hybrids (nars).

Table 1

Variation of Blood Indices with the Age of Camels

	Born 1937				Born 1936			
	n	Number of erythrocytes $M \pm m$	Haemoglobin $M \pm m$	Blood alkalinity in mg % $M \pm m$	n	Number of erythrocytes	Haemoglobin	Blood alkalinity in mg %
1. C. Bactrianus ♂♂	5	10.73	52.4	604	—	—	—	—
2. C. Bactrianus ♀♀	8	10.89±0.69	57.2±2,82	640±1.37	6	11.34	62.3	660
3. C. Dromedarius ♀♀ . . .	—	—	—	—	—	—	—	—
4. Nars — F_1 hybrids ♀♀ . .	6	11.76	62.2	640	5	11.73	59.5	596

	Born 1935				Adult camels			
	n	Number of erythrocytes	Haemoglobin	Blood alkalinity in mg %	n	Number of erythrocytes $M \pm n$	Haemoglobin $M \pm n$	Blood alkalinity in mg % $M \pm n$
1. C. Bactrianus ♂♂	—	—	—	—	—	—	—	—
2. C. Bactrianus ♀♀	9	11.61	59.9±2.11	652	24	10.3±0.2	55.0±0.93	521±7.2
3. C. Dromedarius ♀♀ . . .	2	12.4	62.7	570	18	9.83±0.25	57.3±1.22	560±10.4
4. Nars — F_1 hybrids ♀♀ . .	3	12.9	65.1	633.2	14	11.16±0.43	59.5±1.36	581±11.9

Table 1 shows the composition of the blood of all the camels examined, changing with their age. The reliability of the differences given in this table may be judged by Table 2 which was drawn up on the basis of Student-Fisher's table of probable significance of differences.

Table 2

Probable Significance of Differences in Blood Indices of Adult Female Camels

	Differences between nars and bactrians		Differences between nars and dromedaries	
	Difference and error	Probable significance of difference expressed in percentage	Difference and error	Probable significance of difference expressed in percentage
Number of erythrocytes	0.86± 0.47	93	1.33± 0.49	99.3
Haemoglobin	4.5 ± 1.64	99.4	2.2 ± 1.82	77
Blood alkalinity . .	60 ±13.8	100	21 ±15.8	82

The above table shows that the rate of the probable significance of differences is on the whole very high and only in two instances is below 90, which apparently is due to the fact that an inadequate number of animals, particularly of nars, was examined.

It is extremely significant that in the F_1-hybrid, which is distinguished for its pronounced positive heterosis in regard to working ability and bulk of body, the oxidizing power of the blood is higher than in its parents. The same has been observed in mules by the author and reported in his work now in print. The physiological connection between the higher quality of the blood of our hybrids and the greater working ability of the latter is quite evident. It was Ranke who, by his experiments on rabbits, has shown that muscular efficiency is to a large extent dependent on the oxidizing qualities of blood. In our case it means that the higher quality of the blood of the hybrids is the immediate cause accounting for their higher working ability. Thus, to a certain extent, the results of our studies have brought us closer to the solution of the problem of mechanism of heterosis in such animals.

In order to establish the effect of the variations in the composition of the blood on the productivity of animals of the same species and age, we have divided each of the larger groups of animals into two sub-groups: 1) camels with a live weight exceeding the average for the whole group (plus variants in weight) and 2) camels with a live weight below the average for the group (minus variants in weight); we have computed the figures for each sub-group as shown in Table 3.

Table 3

Change of the Composition of Blood in Female Camels with Live Weight

Groups	Sub-group I. Plus variants in live weight			Sub-group II. Minus variants in live weight		
	Number of erythrocytes in millions	Haemoglobin (Sahli's index)	Blood alkalinity in mg, %	Number of erythrocytes in millions	Haemoglobin (Sahli's index)	Blood alkalinity in mg, %
Nars, 7 years and over . .	11.27	59.2	584	10.4	57.9	580
Dromaderies » » . .	10.42	59.6	564	9.15	53.4	540
Bactrians » » . .	10.26	54.8	500	10.1	54.6	514
Bactrians 6 months old . .	11.63	62.8	676	8.79	50.2	580

Thus, sub-group I (plus variants in live weight) shows considerably higher indices than sub-group II (minus variants in live weight) in all the groups with the exception of the group of adult bactrians. In this latter group the differences are slight while the tendency is the same as in the other groups.

In Table 4 each group of camels of the same age and species has been divided into two sub-groups: 1) those with a content of haemoglobin above the average, and 2) those with a content of haemoglobin below the average. The figures show the live weight of the animals in each case.

This table shows clearly that camels with a higher content of haemoglobin have greater weight and consequently greater working ability.

Finally, in Table 5 we show the rate of growth of young female camels born in 1937 and examined by us when they have reached the age of six months. The camels are divided in two groups, one with a content of haemoglobin above the average and the other with a content below the average.

Table 4

Differences in the Live Weight of the Camels According to Haemoglobin Content of Their Blood

Groups	Live weight in kilograms	
	Sub-group I. Content of haemoglobin above average	Sub-group II. Content of haemoglobin below average
Dromaderies 10 years and under	632	611.5
Dromaderies above 10 years . . .	644	600.5
Bactrians from 4 to 7 years . . .	580	568
» from 8 to 10 years . .	678.2	672
» above 10 years	760	744
Nars $1^1/_2$ years	427	413
» above 10 years	752	664.5

Table 5

Differences in Growth of Young Camels According to Haemoglobin Content of Their Blood

Groups	Live weight in kilograms		
	at birth	at 3 months of age	at 6 months of age
1. Camels with haemoglobin content above average	45	172	221
2. Camels with haemoglobin content below average	41.4	132.8	195.2

Thus, it has been established that those of the young camels which at the time of their examination showed a higher content of haemoglobin weighed more than the others at birth and were developing at a greater rate.

The results of the present investigation support the deductions made by us previously on the basis of experiments with cattle and sheep(2), namely, that a higher oxidizing power of the blood, connected as it is with a more intensive metabolic process, secures a greater rate of development of the animal and a greater live weight upon reaching maturity. Assuming further that the working ability of a camel depends as a rule on the size and consequently on the live weight of the animal we shall be fully entitled to draw the conclusion that animals with a higher oxidizing power of the blood and a greater blood alkalinity possess also greater working ability.

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Received
9. II. 1938.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

ZOOLOGY

THE TEMPERATURE OF WHALES

By B. A. ZENKOVIČ

(Communicated by S. A. Zernov, Member of the Academy; 29. I. 1938)

During the whaling season near the shores of Kamchatka and Chukotka I had the occasion of observing a few cases of whales in agony being taken in tow. This gave me the opportunity of measuring the temperature of five wounded whales. It was not difficult for me to do it since the whales were made fast to the side of the whaler, the deck of which was not more than 0.5 or 0.75 m above water level. Needless to say the crew permitted themselves such liberties only with those whales as were at their last gasp and showed but slight signs of life. However, in one instance (sperm-whale № 192) the whale made fast to the vessel continued to live for another hour.

Method employed. The temperature of the whales was measured by two thermometers: one, copper-mounted, for measuring the temperature of the water surface (№ 1) and another, ordinary medical one (№ 2). The thermometers were inserted into the hole picked with a pike either in the animal's side, nearer the belly, almost at the beginning of the whale's side folds, or sometimes in the belly, depending on the position in which the whale was made fast to the boat. In the case of the sperm-whale the hole is picked in the animal's side a little above the genital orifice, almost near the navel. The wounded whales never reacted when the holes were picked in their bodies. The copper-mounted thermometer with the little glass was almost entirely inserted in the body of the whale, only the ring with the attached cable remaining outside. Thermometer № 2 was completely immersed to a depth of 30—40 cm in the body and extracted by means of a line

Table 1

Temperature of Whales in Agony

№	Registered №	Date of measurement in 1933	Variety of whales	Sex	Thermometer № 1, temperature °C	Thermometer № 2, temperature °C
1	7	30.VI	Fin-whale *(Balaenoptera physalus)*	♂	38.2	38.3
2	25	6.VII	» » »	♀	38.5	38.5
3	89	15.VIII	Humpback-whale *(Megaptera nodosa)*	♂	38.0	38.2
4	170	2.X	Sperm-whale *(Physeter catodon)* . .	♂	38.2	—
5	192	27.X	» » » . .	♂	38.1	38.3

Table 2

Temperature Measurements of Whale Carcasses

№	Registered №	Date of measurement in 1936	Time elapsed from death: hours	Time elapsed from death: minutes	Variety of whales	Sex	Temperature	Number of harpoons in the body	Remark
1	1	29/IV	6	25	Sperm-whale (*Physeter catodon*)	♀	35.2	2	
2	2	29/IV	5	10	»	♀	35.2	2	
3	4	29/IV	4	10	»	♀	36.4	1	Giving suck
4	5	29/IV	4	—	»	♂	37.0	1	
5	11	30/IV	7	30	»	♀	35.7	2	Giving suck
6	12	30/IV	6	05	»	♀	35.6	1	
7	14	30/IV	6	05	»	♀	35.5	1	Pregnant
8	15	7/V	6	—	»	♂	35.6	1	
9	24	7/V	7	30	»	♂	35.5	1	
10	29	12/V	15	—	Blue whale (*Balaenoptera musculus*)	♂	35.6	1	
11	31	14/V	16	—	»	♂	35.7	1	
12	36	15/V	12	—	»	♀	35.7	1	
13	46	20/V	9	—	Fin-whale (*Balaenoptera physalus*)	♂	35.9	2	
14	65	26/V	11	—	»	♂	35.3	1	
15	86	30/V	13	—	»	♂	35.2	1	
16	100	8/VI	3	—	»	♀	35.9	2	Pregnant
17	326	19/IX	2	—	»	♂	36.7	2	
18	330	21/IX	1	30	Grey whale (*Rhachianectes glaucus*)	♂	36.9	1	
19	332	21/IX	3	25	Humpback-whale (*Megaptera nodosa*)	♀	37.1	2	
20	333	21/IX	1	—	»	♀	35.8	6	
21	334	21/IX	4	—	»	♀	35.8	2	
22	341	24/IX	0	35	Grey whale (*Rhachianectes glaucus*)	♀	36.2	2	
23	344	24/IX	0	30	»	♀	35.7	1	
24	349	25/IX	1	30	»	♀	35.2	1	
25	355	25/IX	1	20	»	♂	35.6	1	
26	358	25/IX	1	35	»	♀	36.1	1	
27	361	25/IX	6	—	»	♀	35.9	2	
28	364	26/IX	2	—	»	♀	36.2	1	
29	365	26/IX	2	10	»	♀	36.3	1	
30	367	26/IX	9	—	»	♂	36.1	1	
31	369	26/IX	4	50	»	♀	36.9	1	
32	377	27/IX	1	10	»	♂	37.1	1	
33	387	27/IX	3	—	»	♂	37.3	1	
34	390	28/IX	1	20	»	♂	37.5	1	
35	392	28/IX	—	50	»	♂	37.7	1	
36	468	21/X	3	10	Humpback-whale (*Megaptera nodosa*)	♂	36.5	1	
37	472	23/X	1	20	Sperm-whale (*Physeter catodon*)	♂	36.8	2	
38	476	27/X	1	15	Fin-whale (*Balaenoptera physalus*)	♀	36.9	3	
39	477	27/X	4	—	»	♂	36.5	2	
40	487	1/XI	2	10	»	♂	37.7	2	

made of veins. The thermometers were kept in the animal's body for 10 minutes and the results of each case were recorded. The measurements having been taken with such different instruments, the slight divergence in the readings is therefore explicable. The temperature of the carcasses of the animals was measured by the usual medical thermometers.

Apart from measuring the temperature of the animals during their moments of agony I have also measured the temperature of whale carcasses, taking due account of the time that elapsed from the moment they were killed. The results of temperature measurements of whales in agony are shown in Table 1, and those of carcasses in Table 2.

In analysing Table 1 we observe that the temperature of whales in agony varies in the case of the fin-whale (*B. physalus*) from 38.2 to 38.5° C; in the case of humpback-whale (*Megaptera nodosa*) from 38 to 38.2° C and in the case of the sperm-whale (*Physeter catodon*) from 38.1 to 38.3° C. In one instance, owing to a few convulsive movements of the dying fin-whale, the thermometer was crushed into powder.

Since the temperature of the animals body is sure to be affected by the number of harpoon wounds inflicted on it, I have shown in the table the number of harpoons stuck in its body. As may be seen from Table 2, the temperature of forty whales were measured by me. Of these 1) *Physeter catodon* L. sperm-whales 10 (6♀ and 4♂); 2) *Balaenoptera musculus* Lin.—blue whales 3 (1 ♀ and 2♂); 3) *B. physalus* L.—fin-whales 8 (2♀ and 6♂); 4) *Megaptera nodosa* Bon.—humpback-whales 4 (3♀ and 1♂); 5) *Rhachianectes glaucus* Cope—grey Californian whales 15 (8♀ and 7♂).

Thus, the time elapsed from the moment of the animal death till the moment of measurement of temperature varies between 30 minutes and 16 hours.

As may be observed from Table 2, rigidity in the case of whales is setting in very slowly on account of the blubber which serves as a thermo-isolator and covers the whole body of the whale from the tip of the snout till the fan ends of the tail. We may take it that putrefaction always begins before the final stiffening of the body and therefore these animals in normal conditions do not go through the stage of complete rigidity.

The meat of the blue whale № 11/31, sixteen hours after it was killed, could be used as food and its temperature was 35.7°, but 8 hours later most of it could not longer be used. Usually the meat of a whale is not used for food or canning purposes after the elapse of more than 20 hours from the moment it was killed, since some parts of the carcasse begin to develop ammonia.

In this note I refer exclusively to data obtained by me personally and to animals recently killed. But it is worth while noting that whales, 24, 30 and even 60 hours after they were killed had a temperature approximating 30°C.

On the basis of temperature measurements of five whales in agony and forty carcasses I come to the conclusion that the temperature of whales is not below that of other mammals and that the current belief that whales have a lower temperature is not true.

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Received
29. I. 1938.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

DEVELOPMENT MECHANICS

LENS-BUILDING POWER OF THE EYECUP IN AMPHIBIAE AS AFFECTED BY REPEATED INDUCTION

By N. A. MANUILOVA

(Communicated by J. J. Shmalhausen, Member of the Academy, 15. II. 1938)

A comparative study of the morphogenetic properties of the eyecup at various stages of its development showed a very essential peculiarity of this inductor. The lens-building properties of the eye embryo proved not to be confined to a definite stage of its development ([1],[2]). Experiments showed that not only a well developed cup of a tadpole, but even the cup of an adult amphibia is capable to lens induction, in case a bit of the body epithelium of suitable age is attracted into the sphere of its activity ([3],[4]). The question naturally arised, whether the eyecup is continuously endowed with this power, i. e. whether the effect of its action on the epithelium will remain constant, under the conditions that its inducing properties will be tested many times in rapid succession, or whether it is possible that under such experimental conditions the form-building properties of the cup will gradually be exhausted and even will finally disappear altogether. The latter seems rather improbable, though it should be mentioned among other probabilities.

For the solution of this question it was necessary to undertake such experiments in which the lens-building properties of the cup would be tested several times in succession. Should the first assumption be true, a well differentiated lens would always form after each operation, and the rate of formation should be always the same, irrespective of how many times the cup had already been tested before. If the second assumption were true, the lens could also be formed in each experiment, but the degree of its differentiation, the frequency of occurrence and the rate of formation would vary with each repeated induction. Finally in the last case after a definite number of experiments the cup would be unable to produce any changes in the epithelium that would characterize the formation of the lens.

The experiments were performed on embryos and tadpoles of *Rana ridibunda*. In my experiments I started from the assumption that the eyecup at any stage of development may produce the formation of the lens under adequate conditions. The choice of the stage to begin experiments was therefore of no importance.

I started to operate on embryos in the stage of the tail bud, a stage in which the eye bladder is closely adherent to the lens epithelium, and in the inner layer of the latter an accumulation of nuclei is observed which is cha-

racteristic for the initial stage of lens formation. Therefore at that stage the eyecup must already have produced a certain influence on the lens epithelium, the more so as from our experiments with axolotls it was known that after the removal of the eye embryo at a still earlier stage, when in the presumptive epithelium no changes whatever may be observed, the latter develops into a well differentiated lens(5).

At the first operation I removed the lens epithelium, leaving the cup open, until it was covered with epithelium, bordering the surface of the wound. In two days when a certain effect of the action of the cup on this epithelium could already be expected, a second operation was performed, which consisted in the removal of the epithelium covering the cup and the anlage of the lens, should the latter be formed. The cup either remained open and covered with epithelium, as in the first experiment, or became covered with body epithelium taken from another embryo at the stage of an early tail bud. 3, 4 and 5 days after the second operation a third one was performed. In this operation the epithelium covering the cup was carefully lifted. If the lens anlage had been formed, it was removed and a bit of the body epithelium from the stage of the tail bud was placed inside the cavity of the cup. Thus, these operations were performed on each embryo. After the third operation the cup exerted its effect on the epithelium for the 4th time, since, as we already have mentioned, it first affected the epithelium of the lens as early as before the first operation.

In the operation it was necessary to note the position of the lens material for each embryo at the moment of operation. As the macroscopic examination proved to be unsufficient in order to find out the exact result of the influence of the cup on the epithelium at the moment of each operation, we were obliged to fix a part of embryos during each operation to study them afterwards in detail in sections. Owing to that we had to operate a great number of embryos in each set, as 1) it was important to perform all the three operations on the same embryo, and 2) it was necessary to fix a part of the embryos, so that the number of embryos in each subsequent series gradually decreased.

Results Obtained

The second operation was performed two days after the first. A histological study of the embryos fixed by that time, i. e. of those operated once, while the cup was acting for the second time, showed that the lens on the operated side developed in the same way as on the control side. The cut of the lens anlage exhibited either a multilayered thickening of the epithelium, or an empty vesicle. The results of the histological examination agreed with those of the macroscopic one done during operation. The third operation followed the second in two, three and four days. At the same time those embryos on which two operations had been performed and the cup acted for the third time, were fixed. We shall analyse here only those embryos in which the cup was covered after the operation with the head epitelium, while among embryos with body epithelium transplanted in the eye no single case of lens-formation could be established.

Two days after the second operation the lens developed in all embryos. On section the anlage of the lens presented either a thickening of the epithelium or a small vesicle, occasionally with an anlage of the fibrous part. These lenses are not to be compared with those on the unoperated side of the same embryo, as the second operation was performed at the moment when fibrous elements differentiated on the unoperated side. It should, however, be noted, that the lenses on the operated side are too small and bear traces of a defective development. The eyecups, in spite of two operations, are at the

same stage of development as on the unoperated side. During fixation three or four days after the operation the primordium of the fibrous part is already being formed and the fibres begin to differentiate. Yet the lens is still small, its epithelial layer is thickened and the cell distribution is irregular. In one embryo out of the whole lot which had been, by chance, fixed ten days after the operation, the lens contained two vacuolis which clearly indicate the beginning of the degeneration process.

Therefore at the moment of the third operation the lens already existed. As a matter of fact, in the diary we noted that at the moment of the third operation the lens was present not in all embryos. As it was proved by histological examination, the developed lenses are very small and show signs of degeneration.

The third operation was the last one. After it the embryos were fixed in 3, 4, 5, 6 and 7 days respectively. It should be noted that the results of the operation were the same irrespective of the date of fixation. Alongside of well differentiated lenses, differring from the lenses on the unoperated side by nothing but smaller size and occasionally by an irregular structure of the epithelial layer, embryos could be observed, in which very small, irregularly shaped lenses developed, which may be called lentoids.

In the lenses of several embryos already differentiating into epithelial layer and fibrous elements, we observed vacuoli. In 6 embryos out of 40 the lens did not develop at all. These results were obtained in spite of the fact that the cups of these embryos developed on the unoperated side too, differing only in their smaller size.

To check the experiment made on thrice operated embryos, a control experiment was undertaken, viz., bits of body epithelium were transplanted into the cavity of the cup deprived of lens in embryos at the same developmental stage as the experimental embryos toward the moment of the third operation. Thus the cup of these embryos was tested only for the second time. Using the same rate of fixation as in experimental animals, the results obtained were different. In all embryos without exception the transplanted epithelium developed into a well differentiated lens differing only by its smaller size from the lens on the unoperated side.

From the data briefly exposed here it follows that the form-building power of the cup changes with the rate of its action on the epithelium. The cup cannot continuously secure the development of a normal, well differentiated lens. It is especially made obvious by the comparison of the results of the transplantation of the body epithelium into the cavity of the cup, which is acting for the fourth time (3rd operation) or only for the second (control of the 3rd operation). In spite of the fact that in both experiments the properties of cups being at the same developmental stage and equally well developed were tested, using embryonal epithelium of the same age, different experimental effects were obtained. We should not forget, however, that the control set differred from the experimental one not only by the fact that in the former the cup was acting for the second time, but also by a greater interval between the stages, when it secures the development of the lens from the lens epithelium in the usual course of development and from the body epithelium in the experimental one. In each induction the lens-building power of the cup is exhausted and may afterwards be restituted. Yet the process of regeneration requires a definite period of time, which obviously exceeds that separating the operations in my experiments. We could suppose that the general state of the embryo grows worse owing to frequent surgical interventions and thus produces a negative effect on the inducing power of the cup. But we could observe no anomaly in the development of the operated embryos and the cup itself maintained its normal structure

on the operated side, similar to that on the unoperated side of the same embryo.

It is difficult to say at present what is the cause, or are the causes leading to the exhaustion of the form-building power of the cup. The work is proceeding in this direction and further experiments will enable us to approach nearer to this phenomenon.

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Received
28. II. 1938.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XVIII, № 9

DEVELOPMENT MECHANICS

INVESTIGATION OF THE MORPHOGENETIC PROPERTIES OF THE EYECUP IN TAILLESS AMPHIBIAE

By N. A. MANUILOVA, A. I. MACHABELI and T. A. SIKHARULIDZE

(Communicated by J. J. Shmalhausen, Member of the Academy, 15. II.1938)

Experimental investigation of the eye development was first concerned with only one fundamental question: does the lens develop independently of the eye embryo having been formed or having not, or is the former process dependent upon the latter and the lens did not appear as anlage, nor develops if the eye embryo has been extirpated.

The first experiments of Spemann(1) with the extirpation of the eye material in the neurule of *Rana temporaria* have shown that the lens anlage does not form in the absence of the material of the cup. Spemann came thus to the conclusion that the formative influence of the cup is typical for the development of the crystalline lens. A further experimental study of morphogenetic properties of the eyecup in amphibiae has shown the dependence of the lens development on the eye embryo to be differently expressed in different species. There is a gradual transition from species in which a well differentiated lens develops on the neurula after the removal of eye material to such in which no anlage of the lens forms after the operation.

The formative influence of the eyecup is, however, maintained in all species, irrespective of their being able or not to form the lens anlage in absence of the eyecup.

All these experiments concerned with the investigation of the morphogenetic activity of the cup refer to the stage, when the lens anlage is formed in the typical course of development. In connection with these works the question arose whether the form-building influence of cup is limited within the stage of lens anlage forming in the typical course of development, or whether the ability of the cup to induce the lens is maintained during the further development. As early as in 1905, in one of his papers Spemann(2) assumed that the inducing properties of the eye embryo are not confined to a definite stage of its development. A systematic study of the lens-forming properties of the eyecup during the later stages, undertaken by Manuilova, showed that the ability of the cup to induce the lens was not determined by the period, when its influence is indispensable for the lens anlage to form in the course of normal ontogenesis. The cup retains its form-building influence on the epithelium even after its function with respect to the anlage of a normal lens has been in the main fulfilled(3). The original properties of a late cup were tested either on the epithelium covering the cup after the extirpation of the lens material or on the epithelium of the body, transplanted to the cup.

These experiments show that though a late cup maintains its inducing properties, nevertheless its lens-forming power changes with age, viz., the more advanced is the stage of the cup, the more defective is the lens primordium induced by it. The last conclusion proved to be wrong; further experiments showed that the development of defective lenses was conditioned not by the changes of the inducing properties of the cup with age, but by the changes in the conditions of its action on the epithelium. At the stage of the tail bud, when the lens is generally formed, the eye embryo in the shape of an empty bladder comes into close contact with the epithelium, while at the later stages the bladder is transformed into a concave two-walled cup—the layer of the retina is disjunct from the epithelium covering the cup and even stands off at a certain distance from the latter.

This moment is apparently of great importance for induction. Having taken this fact into consideration, we modified the technique of the experiment, the epithelium was transplanted not on the cup but into its cavity, the sphere of its maximum influence. Under these conditions a well shaped concave cup proved to induce an adequate lens differentiating into epithelial layer and fibrous mass. From this fact Manuilova assumed that the eyecup retains its inducing properties for a long period, perhaps for ever. Yet this assumption required experimental evidence. We continued these experiments with the purpose to test the morphogenetic properties of the cup at still later stages. Parallel to our investigations, similar experiments on big tadpoles and even on adult forms were undertaken by Nikitenko at the Institute of Experimental Morphogenesis. His data(4) confirmed the assumption that the cup maintains its determining properties throughout the ontogenesis. Nikitenko's assertion that Manuilova arrived to a conclusion lacking accuracy with regard to the «cessation of determinative influence exerted by the eyecup towards the end of its invagination period», is absolutely wrong. Even in her early papers on lens-forming properties of the cup changing with age, Manuilova does nowhere mention the cessation of the determining influence of the eyecup, only pointing out the fact that «the determining factors of the cup producing the formation of the lens in the embryonic epithelium, maintain their inducing property, at least they do so till the stage of disjunction of the normal lens from the epithelium», i. e. at the latest stage tested. In the last work reported on Dec. 14, 1936, at the Institute of Experimental Morphogenesis, with the data of which Nikitenko seems not to be familiar, Manuilova transplanted the epithelium not in the cup, as in the first experiments, but into its cavity, and succeeded in obtaining the induction of a well differentiated lens. This made her suggest that the inducing power once acquired seems to be maintained by the eye embryo for ever.

The presence of the lens-forming ability in the cup of adult forms of amphibiae is an essential factor for the investigation of the process of restitution of the crystalline lens by its formation out of the upper edge of the iris. Till now we do not know the factors conditioning the important and complicated process of the restitution of organ. For the first time the fact of the restitution of the lens was observed in triton by Colluchi when investigating the regenerative power of the eye. The first detailed description of this process belong to Wolf, therefore the formation of the lens from eye material was called the Wolf-regeneration of the lens. We shall not dwell upon experiments concerning mostly the descriptive side of this process. We shall only point out that an experimental investigation of the process of regeneration of crystalline lens in various amphibiae showed that in tailless amphibiae the possibility of the regeneration of the lens is confined to a comparatively early stage of ontogenesis, while in the triton it takes place in adults too. This different ability to regeneration in tailless and tailed

amphibiae was the starting point of our attempts to find out the factors accounting for such phenomenon. But before attempting to throw light on the mechanism of regeneration of the lens from the edge of the cup, we considered it necessary to determine the stage, during which the regeneration of the lens becomes impossible in tailless amphibiae.

We shall briefly expose the data of our experiments made to establish: 1) the morphogenetic properties of the eyecup in grown tadpoles and 2) the limit stage at which the material of the eye loses its ability for the regeneration of the lens in tailless amphibiae.

Both series of experiments were performed on tadpoles of *Rana ridibunda* and *Bufo viridis*. The first series of experiments consisted in the extirpation of the lens at different stages of development in tadpoles and in a subsequent transplantation of bits of embryonic body epithelium (tail bud) into the cavity of the cup. In the second series we limited ourselves to the extirpation of the lens at various stages of development of tadpoles, in order to trace up the changes of the upper edge of the iris in lensless animals. The stages of the recipients were the same in both series. 1) Tadpoles with inner gills, the buds of the extremities not yet appeared. Body length 10—11 mm. 2) Big tadpoles with inner gills. The appearance of the buds of the hind legs. Body length 25—26 mm. 3) Tadpoles with differentiated hind legs. 4) Tadpoles with all the legs differentiated. At the moment of operation the tail was represented in the form of a fin.

The results of the experiments concerning the investigation of the morphogenetic properties of the eyecup at later stages of development showed that the cup in big tadpoles maintains its ability to induce the lens.

The embryonic epithelium of the body develops into a well differentiated big lens, if it has been transplanted at the place of the removed one, namely in the cavity of the cup in tadpoles with well differentiated hind legs. Yet a comparison of the result of the experiments, according to stages, shows that after the transplantation of the body epithelium into the cavity of the cup at earlier stages, the lens is formed in almost all the operated animals, while in tadpoles with well differentiated hind legs the ratio of lens formation is considerably reduced. 2—3 days after operation the lenses already differentiate into epithelial layer and fibrous mass.

We can judge of their origin from the transplanted tissue by the fact that the epithelial layer of some lenses remains connected with the remnants of transplanted bit. In many cases the cells of the epithelial layer of the lens present a random distribution and do not form a regular row as usual. Moreover, occasionally cells were found in the lenses, between the epithelial layer and the fibrous mass, which contained pigment. These cells present the remains of the transplanted part. None of these phenomena was observed in the formation of the lens from the edge of the cup. With respect to lenses fixed a long time after the operation (39 days) it is hard to judge of their origin, because the remnants of the transplantate are usually completely resorbed by that time, abnormalities in the structure of the epithelial cells smoothed out. But from the few cases where the originating of the lens from the transplantate has been established beyond doubt, we may conclude for the presence of a form-building ability in the eyecup of big tadpoles.

The greater part of experiments was performed on tadpoles of *Rana ridibunda*. In tadpoles of *Bufo viridis* the transplantation of the body epithelium was performed only into the cavity of the eyecup of the tadpoles with differentiated hind legs. The experiments gave positive results, the same as in *Rana ridibunda*.

As to the ability of the eyecup for restitution of the lens, the results obtained were different for *Rana ridibunda* and *Bufo viridis*. While in the for-

mer the lens proved to regenerate even in tadpoles with two pairs of well dif ferentiated legs (several cases observed), no changes in the upper edge of iris at the same stage in *Bufo viridis* could be detected. We did unfortunately not succeed in extirpating the lens in *Bufo viridis* at earlier stages, thus we do not possess sufficient material to judge of the possibility of the lens regeneration at earlier stages of development.

We can as yet advance no adequate interpretation of the conflicting results obtained in the two forms. As shown above, the cup of the big tadpoles of *Bufo viridis* is not devoid of the ability for the induction of a lens from the epithelium. Therefore if the formation of the lens from the edge of the cup is conditioned by the form-building influence of the cup, we must look for the cause of the absence of the lens in the tadpoles of *Bufo viridis* in the material which is subjected to the influence of this cup. But the solution of this problem will constitute the next step of our experiments.

The impossibility of the formation of the lens from the cup edge in the tadpoles of *Bufo viridis* gives us additional ground to assume that all lenses, formed by the tadpoles of this species after the transplantation of the epithelium into the cavity of the cup of big tadpoles, have developed out of the epithelium.

Thus the results of the experiments given above enable us to draw the two following conclusions:

1. The eycup of the tadpoles with well differentiated hind legs maintains the ability to induce the lens both in *Rana ridibunda* and in *Bufo viridis.*

2. The regeneration of the lens from the cup edge in tadpoles with two pairs of well differentiated extremities has been observed only in *Rana ridibunda* (individual cases), while in *Bufo viridis* the same operation, at the same stage of development, was not accompanied with any changes in the upper edge of the iris.

The Embryological Station
of the People's Commissariate of
Public Education.
Georgia, Tbilisi.

Received
22. II. 1938.

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